

Draft

Mercury Total Maximum Daily Load Development for the North Fork Holston River, Virginia



Prepared for: Virginia Department of Environmental Quality

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Draft v20

Submitted by:



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EXECUTIVE SUMMARY

Background

High levels of mercury have been detected in fish tissue in the North Fork Holston River for the past three decades. This has led to the inclusion of the river in a list of water bodies that require a Total Maximum Daily Load (TMDL) called the 303(d) list in 1996. The creation of this list was mandated by the Clean Water Act (CWA) that became law in 1972. A TMDL is a "pollution budget" that sets limits on the amount of pollution that a water body can tolerate and still maintain water quality standards. The agency handling this effort in Virginia is the Virginia Department of Environmental Quality (DEQ). The current report is the first step in this cleanup plan. During the TMDL study, sources of mercury are identified and quantified. Computer models are used to assess the impact of mercury loading on the mercury levels within the river. The TMDL then presents a set of recommendations to bring the levels of mercury in fish tissue down to an acceptable amount.

Fish consumption advisories have been in place by the Virginia Department of Health warning people not to eat fish caught in the river since the 1970s. The length of the river impacted by this advisory extends from near Saltville, Virginia to the Virginia/Tennessee state line. The over exposure to mercury can cause kidney, brain and nerve damage, especially in children (DEQ, 2009).

A portion of the mercury was introduced into the river during the 1950s and 1960s due to industrial activities. Olin Corporation operated a manufacturing facility that produced chlorine and caustic soda. Mercury was used in the process and some of the mercury was discharged into the river. At the time, the discharge of mercury was not illegal and no one realized that mercury was harmful. In 1972, the manufacturing of chlorine and caustic soda at the Saltville plant stopped and the plant was dismantled and demolished. Olin signed a consent order with Virginia State Water Control Board in 1982 to implement remedial actions at Pond 5, FCPS, and river along with a monitoring program. Olin completed several remedial activities including dredging contaminated sediments from the river and capping the disposal sites known as Pond 5 and Pond 6. These

remedial actions reflected positively on the concentration of mercury in fish tissue. Other sources of mercury in the North Fork Holston River area that contribute to the problem come from atmospheric deposition. Mercury is released into the atmosphere due to fossil fuel burning and a portion of that released mercury settles on the ground surface and on water bodies directly.

The watershed is predominantly forested (over 70%) with a fair amount of pasture land and approximately four percent developed. The NFHR flows northeast to southwest from the headwaters in Bland and Tazewell counties through Smyth, then Washington, then Scott counties and crosses the Virginia-Tennessee State Line near Weber City, Virginia. The NFHR then flows into the Holston River a few miles downstream inside the state of Tennessee.

Sources of Mercury

Mercury in the North Fork Holston River comes from different sources. Some of these sources are point sources with the discharge of permitted facilities. Other sources are not as defined and come from large swaths of land in what is known as non-point sources.

Field measurements from four sources related to the former chlorine production plant were used in the analysis. These sources were the former chlorine plant site (FCPS), groundwater from Pond 5, groundwater from Pond 6, and the treatment plant constructed to handle outflows from Pond 5 and 6.

The top soil within the study area contains mercury. The watershed was divided into two areas, the first area contains the top soil within the floodplains adjacent to the North Fork Holston River. The floodplains contain mercury as a result of atmospheric deposition, as well as, from the settling of sediment that was contaminated by the chlorine production facility after a flooding event. The second area is the remainder of the watershed with levels of mercury in top soil generally less than those impacted by the chlorine plant. Mercury from these two areas ends up in the river during storm events when mercury that is attached to the soil washes in with sediment. Measured concentrations from these areas were used to generate input for the computer model.

Atmospheric deposition of mercury is mainly due to coal burning since coal naturally contains mercury. Some of the mercury released from the burning of coal falls back on the ground and water surfaces. The amounts deposited on the North Fork Holston River area may not necessarily be all from plants within Virginia since mercury in the atmosphere can travel hundreds and even thousands of miles before settling. Measurements from two atmospheric deposition monitoring sites surrounding the study area were used to generate input for the computer model that reflects the contribution of atmospheric deposition.

When rain or snow falls, some water penetrates the ground surface. A portion of this water, called interflow, flows laterally and enters streams. The remaining portion, called groundwater, penetrates deeper into ground with parts of it emerging into streams some distance away. Both of these forms of flow contain mercury. The source of mercury is either from atmospheric deposition or picked up by water flowing downwards. Both of these sources of mercury were accounted for in the computer model. The exact concentrations were obtained through calibration of the model since no sufficient measurements were available.

Computer Modeling

Once sources were quantified, a computer model was developed to simulate the processes of mercury transport to the river. Besides accounting for the sources of mercury, the computer model also mimics the real physical world. This is accomplished by including parameters in the model that account for soils, land use, slopes, climatic conditions, and the stream connectivity. The model is capable of simulating the interaction between rainfall, soil transport, mercury transport, and the resulting concentration of mercury within the river. The model simulates the transport of water, sediment, and mercury from land surfaces to the river and has additional components that handle the fate of mercury once it is in the river. The accuracy of the model is tested by comparing model predictions of flow, sediment, and mercury with actual observed samples collected throughout the drainage area.

Existing Conditions

Once the model was calibrated for hydrology, sediment, and mercury, the model was used to simulate the existing conditions in the watershed. Existing conditions were obtained as a result of measurements in the field, information obtained about point sources as well as the results of mercury calibration. Under existing conditions, the model simulation indicated that 21,655 grams of mercury (approximately 48 lbs) enter the river each year. Figure E.S.1 shows the relative contribution of various sources of mercury towards this average annual load.

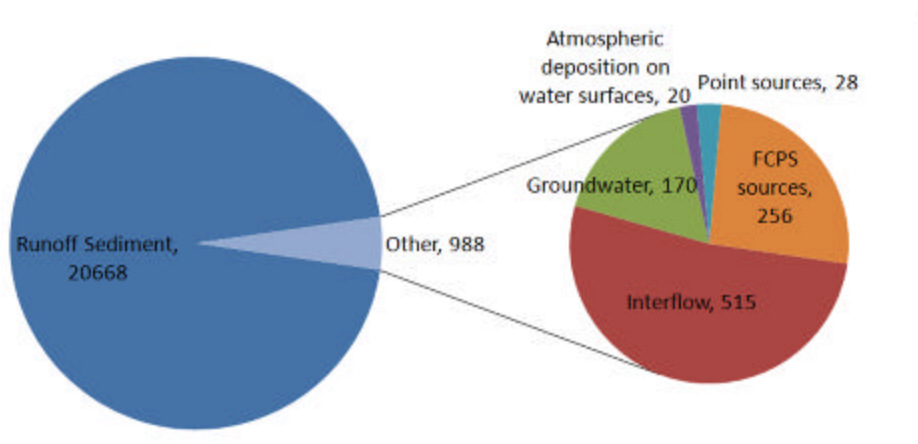


Figure E.S.1 Source contribution of mercury under existing conditions in grams per year.

Allocation

During allocation, reductions in mercury sources were simulated until mercury concentrations in the river met the endpoint. This process resulted in a set of recommended reductions to different sources in order to meet the water quality goals.

In summary, reductions of approximately 20% to concentrations of mercury in atmospheric deposition and interflow were recommended. These amounts are in line with the Environmental Protection Agency's (EPA) expected reductions to mercury in atmospheric depositions due to emission regulations. A higher reduction of 80% is needed from mercury with runoff. Reducing the amount of sediment that gets washed off to streams and rivers will help in achieving this goal since mercury attaches strongly to

sediment. Finally, a 52% reduction in point source and FCPS related sources is needed. The combined impact of all of these reductions is expected to bring the concentrations of mercury in fish tissue down to fish advisory level of 0.3 mg/kg.

Based on these reductions, the amount of mercury that can enter the North Fork Holston each year while the mercury levels stays at or below acceptable levels is 4,867 grams (under 11 pounds). Out of this amount, approximately 13 grams come from permitted point sources while the rest comes from the remaining non-point sources. Table E.S.1 shows the contribution of various sources under existing conditions and after allocation.

Table E.S.1 Mercury loading under existing and allocated conditions.

Source	Existing Load (grams per year)	Percent Reduction	Allocated Load (grams per year)
Hg in runoff sediment	20,666	80%	4,133
Hg in interflow	515	20%	412
Hg in groundwater	170	0%	170
Hg in atmospheric deposition	20	20%	16
Hg in point sources	28	52%	13
Hg in FCPS sources	256	52%	123
Total	21,655	78%	4,867

The resulting TMDL which is the combined mercury load from point sources (WLA) and nonpoint sources (LA) along with a margin of safety is shown in Table E.S.2. The margin of safety accounts for uncertainty in parameter estimation. The margin of safety was accounted for implicitly in this project by making conservative assumptions and estimates.

Table E.S.2 Total maximum daily load of mercury expressed as grams per year.

WLA (grams per year)	LA (grams per year)	MOS	TMDL (grams per year)
13	4,854	<i>Implicit</i>	4,867

Where Do We Go From Here?

This report will be made available to the public. The public will be invited to attend a meeting where the findings will be explained and everybody will be given a chance to

comment on the report. The report will then be submitted to EPA for approval. An implementation plan will then be developed where the reductions recommended here will be translated into control measures. The final stage of the process is to implement these measures in an adaptive way and continue monitoring to assess progress. The major challenge that the state faces is the lack of available options to control out-of-state sources of atmospheric deposition.

ABBREVIATIONS AND ACRONYMS

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BMP	Best Management Practice
BST	Bacterial Sources Tracking
CAIR	Clean Air Instate Rule
CAMR	Clean Air Mercury Rule
CWA	Clean Water Act
DEM	Digital Elevation Models
DEQ	Department of Environmental Quality
EPA	Environmental Protection Agency
ERA	Ecological risk assessment
FCPS	Former chlorine plant site
Hg	Chemical form of Mercury
HHRA	Human Health Risk Assessment
HSPF	Hydrologic Simulation Program – Fortran
IBI	Index of Biotic Integrity
IMPLND	An HSPF application module which simulates the water quantity and quality processes which occur on an impervious land segment
IP	Implementation Plan
LA	Load Allocations
MACTEC	MACTEC Engineering and Consulting, Inc.
MOS	Margin of Safety
NFHR	North Fork Holston River
NCDC	National Climatic Data Center
NPL	National Priorities List

ABBREVIATIONS AND ACRONYMS

PERLND	An HSPF application module which simulates the water quantity, and quality processes which occur on a pervious land segment
RI/FS	Remedial Investigation/ Feasibility Study
SWCB	State Water Control Board
TAC	Technical Advisory Committee
TMDL	Total Maximum Daily Load
TSS	Total Suspended Solids
UAA	Use Attainability Analysis
USEPA	United States Environmental Protection Agency
USGS	United States Geological Survey
VADEQ	Virginia Department of Environmental Quality
VDH	Virginia Department of Health
VPDES	Virginia Pollutant Discharge Elimination System
WLA	Waste Load Allocations
WQMP	Water Quality Management Plan
WQMIRA	Water Quality Monitoring Information and Restoration Act

1. INTRODUCTION

1.1 Regulations Background

One of the goals of the Clean Water Act (CWA) of 1972 is that all U.S. streams, rivers, and lakes would meet certain water quality standards. The CWA also demanded that states conduct monitoring to identify waters that are polluted or do not otherwise meet standards. Through this program, the state of Virginia has found that the North Fork Holston River does not meet state water quality standards for fish consumption. The length of the impairment is roughly 80.4 river miles and extends from above the former Olin Mathison Plant site near Saltville, Virginia down to the Virginia/Tennessee State Line.

When a waterbody fails to meet standards, the waterbody is listed in the current Section 303(d) report as requiring a Total Maximum Daily Load (TMDL). Section 303(d) of the CWA and the U.S. Environmental Protection Agency's (EPA) Water Quality Management and Planning Regulation (40 CFR Part 130) both require that states develop a Total Maximum Daily Load (TMDL) for each pollutant. A TMDL is a "pollution budget" for a waterbody; that is, it sets limits on the amount of pollution that a waterbody can receive and still meet its designated use. In order to develop a TMDL, background concentrations, point source loadings, and nonpoint source loadings are considered. A TMDL accounts for seasonal variations and must include a margin of safety (MOS).

Once a TMDL is developed, and approved by EPA, measures are taken to reduce pollution levels in the waterbody. Virginia's 1997 Water Quality Monitoring, Information and Restoration Act (WQMIRA) states in section 62.1-44.19:7 that the "*Board shall develop and implement a plan to achieve fully supporting status for impaired waters*". The TMDL Implementation Plan (IP) describes measures, such as the use of better treatment technology and the installation of best management practices (BMPs), that should be implemented in a staged process. Through the TMDL process, states establish water-quality based controls to reduce pollution and meet water quality standards.

1.2 Background and History

High levels of mercury in fish tissue were measured at various locations along the North Fork Holston River (NFHR). The impaired segment extends for roughly 80.4 river miles between Saltville and the Virginia/Tennessee State Line and has been in effect since the 1970s. The fish consumption advisory is a “do not eat” advisory prohibiting the consumption of any fish caught within the impaired segment.

A major source of mercury in the river is from atmospheric deposition mainly due to coal burning. Mercury deposition either falls directly on water surface or on land surface where it mixes with soil and gets washed off to the river with sediment during rainfall events. Another historically major source of mercury in the NFHR are the amounts introduced to the river at the Saltville Site. This was a manufacturing facility for 78 years from 1894 to 1972. Operations included a soda ash plant (1894 to 1970) and a mercury cell chlorine plant (1950 to 1972). All plant operations ceased by 1972 and demolition of the Former Chlorine Plant Site (FCPS) was completed in June 1973.

The Saltville Site was added to the National Priorities List (NPL) in 1982. Olin signed a Consent Decree with EPA in 1988 to implement Interim Remedial Measures and a Remedial Investigation/Feasibility Study (RI/FS). The site was divided into three Operable Units (OU-1 Interim Remedial Measures, OU-2 Source Area Investigations, and OU-3 North Fork Holston River (NFHR) Investigations).

Several remedial activities took place to address this problem. Most notably was the excavation of contaminated river sediment in 1982. In addition, a treatment plant was constructed to process effluent from a 75 acre pond (Pond 5) in 1994. A cap was placed on Pond 5 and a cover was added to another 50 acre pond (Pond 6) in 2001 - 2002.

These actions resulted in improved water quality over time. A decline was observed in the concentration of mercury in fish tissue. Reductions in mercury and methylmercury concentrations in Asiatic clams, megaloptera, and crayfish have decreased between 58 percent and 76 percent between 1990 and 2002. Smallmouth bass filet average mercury concentrations decreased approximately 35 percent between 2003 and 2007. An Index of Biotic Integrity (IBI) study performed [by MACTEC] in 2005 showed expected species

composition and diversity for benthic macroinvertebrates. Compared to historical IBI data, 2005 showed marked improvements in abundance and diversity of fish and macroinvertebrates. NFHR surface water samples collected in 2008 adjacent to Ponds 5 and 6 were below surface water quality criteria. Groundwater concentrations from Ponds 5 and 6 continue to decrease since Ponds 5 and 6 were capped. Fish tissue and sediment concentrations continue to decrease over time at a rate of approximately 2 to 4 percent per year. A complete description of history of site and remedial actions may be found in Appendix A.

1.3 North Fork Holston River Watershed Characteristics

The NFHR (USGS Hydrologic Unit Code 06010101) watershed is approximately 450 thousand acres and spans over portions of Scott, Washington, Smyth, Bland, Tazewell, and Russell counties. This watershed is a part of the Tennessee/Big Sandy River basin, which drains via the Mississippi River to the Gulf of Mexico. The location of the watershed is shown in Figure 1.1.

The watershed is predominantly forested (over 70%) with a fair amount of pasture land and approximately four percent developed. The NFHR flows northeast to southwest from the headwaters in Bland and Tazewell counties through Smyth, then Washington, then Scott counties and crosses the Virginia-Tennessee State Line near Weber City, Virginia. The NFHR then flows into the Holston River a few miles downstream inside the state of Tennessee.

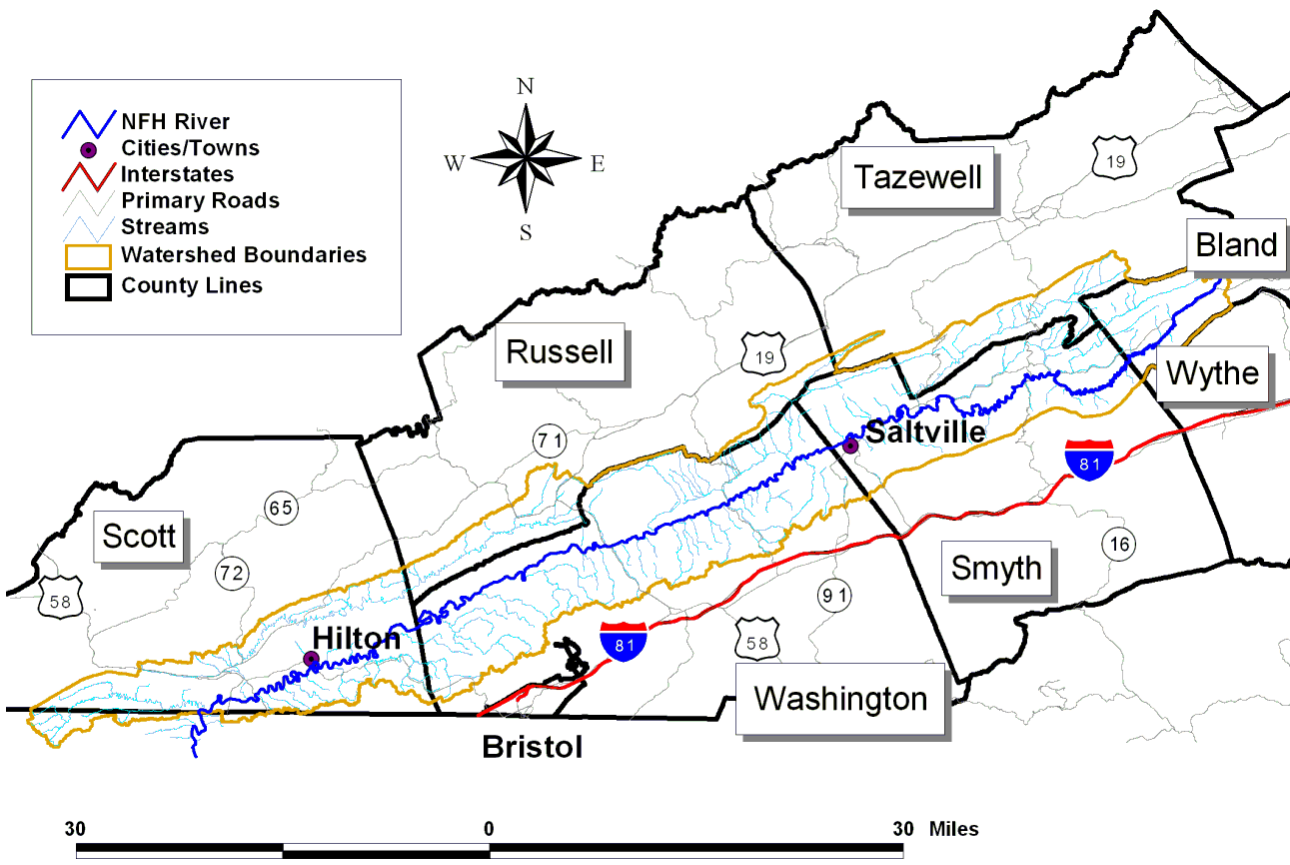


Figure 1.1 Location of the North Fork Holston River watershed.

The North Fork Holston River watershed is entirely located within the level III Ridge and Valley ecoregion in four different level IV subsets: Southern Limestone/Dolomite Valleys and Low Rolling Hills (39% of watershed), Southern Sandstone Ridges (38% of watershed), Southern Shale Valleys (17% of watershed), and Southern Dissected Ridges and Knobs (6% of watershed). The level III ecoregion is described by Purdue University as: “This northeast-southwest trending, relatively low-lying, but diverse ecoregion is sandwiched between generally higher, more rugged mountainous regions with greater forest cover. As a result of extreme folding and faulting events, the regions roughly parallel ridges and valleys have a variety of widths, heights, and geologic materials, including limestone, dolomite, shale, siltstone, sandstone, chert, mudstone, and marble. Springs and caves are relatively numerous. Present-day forests cover about 50% of the region. The ecoregion has a diversity of aquatic habitats and species of fish.” (www.hort.purdue.edu/newcrop/cropmap/ecoreg/descript.html).

The North Fork Holston River watershed is comprised of many different SSURGO (Soil Survey Geographic) soils. The four most prominent soil complexes are: Westmoreland silt loam, Lily loam, Carbo-Rock outcrop complex, and Gilpin-Shelocta silt loams (NRCS, 2008). The Westmoreland series (5% of the watershed) consists of deep, well-drained, moderately permeable soils. This soil was formed from weathered sandstone, siltstone and limestone. The land with this series ranges in slope from 0 to 70 percent (NRCS, 2008). The Lily series (4% of the watershed) consists of moderately deep, well-drained, moderately-rapid permeable soils. This soil was formed from weathered sandstone with siltstone. The land with this series ranges from a 0 to 65 percent slope (NRCS, 2008). The Carbo series (3% of the watershed) consists of moderately deep, well-drained, slowly permeable soils. This soil was formed from weathered limestone bedrock. The land with this series ranges from a 2 to 65 percent slope (NRCS, 2008). The Gilpin series (2% of the watershed) consists of moderately deep, well-drained, moderately permeable soils. This soil was formed from weathered shale, siltstone, and sandstone. The land with this series ranges from a 0 to 70 percent (NRCS, 2008).

The NFHR watershed climatic conditions during the period from 1948 to 2009 in Saltville, Virginia (NCDC station# 447506) were characterized by an average annual

precipitation of approximately 44 inches, with half of this amount occurring during the May through October growing season (SERCC, 2009). Average annual snowfall is 17 inches, with the highest snowfall occurring during January (SERCC, 2009). The highest average maximum temperature of 85.2 °F occurs in July, while the lowest average minimum temperature of 23.9 °F occurs in January (SERCC, 2009).

1.4 North Fork Holston River Mercury Impairment

An 80.40-mile stretch of the North Fork Holston River was initially listed as impaired for fish consumption (mercury) on the 1996 303(d) list. This segment includes the mainstem of the North Fork Holston River from the Olin plant site in Saltville, Virginia to the Virginia/Tennessee state line. Mercury (Hg) contamination in fish tissue prior to 1982 led to a ban on fish consumption. Sediment sampled from the North Fork Holston River show mercury exceedances of the consensus probable effect concentration (PEC) 1,060 ug/Kg. However, since 2002, Hg in sediment downstream of river mile 67 has not exhibited concentrations above PEC.

In the 2002 303(d) list, the North Fork Holston River was divided into 7 separate segments all of which are impaired for mercury contamination in fish tissue. Several of the following segments have multiple impairments; however, this study only deals with the mercury contamination in fish tissue. The most upstream segment from river mile 85.40 in Saltville, Virginia to Robertson Branch is 1.84 miles. Next, from Robertson Branch to Tumbling Creek is 4.79 miles. Mercury values in sediment samples exceeded the PEC at station 6CNFH080.43. The following downstream segment extends from Tumbling Creek to Brumley Creek and is 14.64 miles long. The segment from Brumley Creek to Cabin Creek is 1.9 miles long. Further downstream, from Cabin Creek to Cove Creek (35.42 miles), shows mercury in fish tissue impairment. Fish tissue and sediment samples at station 6CNFH039.18 exceeded limits. At stations 6CNFH059.65 and 6CNFH060.93 sediment samples had high mercury levels. Also listed in 2002, the segment from Cove Creek to Big Moccasin River is 18.76 miles long. The most downstream impaired segment is 5.29 miles long from Big Moccasin River to the Virginia/Tennessee state line.

All of the North Fork Holston River segments remained on the 2004 303(d) list for a fish consumption (mercury) impairment. The only changes in the 2004 report were updates to the segment lengths of the two most downstream segments. The Cove Creek to Big Moccasin River segment was updated to a length of 18.39 miles. The Big Moccasin River to the Tennessee state line segment was updated to a length of 5.81 miles.

There were multiple changes and updates in the 2006 303(d) list; however the entire length of the North Fork Holston River from Olin plant site to the Tennessee state line remained listed as impaired for fish consumption (mercury). The segment from Robertson Branch to Tumbling Creek was updated to a length of 4.83 miles. In this segment, mercury values were above VADEQ screening values in fish tissue at station 6CNFH078.55. The length of the segment from Tumbling Creek to Brumley Creek was updated to 14.79 miles. In the Brumley Creek to Cabin Creek segment at station 6CNFH060.93, mercury in sediment was above PEC (1.54 mg/kg). The segment from Cabin Creek to Cove Creek (35.42 miles) was divided into five separate segments in the 2006 list. First, from Cabin Creek to Little Moccasin Creek (2.82 miles) mercury was detected in sediment. The four other new segments are: Little Moccasin Creek to Smith Creek; Smith Creek to Abrams Creek; Abrams Creek to Livingston Creek; and Livingston Creek to Cove Creek. The Cove Creek to Big Moccasin River segment was updated to a length of 18.73 miles. The Big Moccasin River to the Tennessee state line segment was updated to a length of 5.31 miles. In this segment at station 6CNFH060.93, fish tissue tested above PEC for mercury.

Although the North Fork Holston River was separated into many segments during the different 303(d) lists, the entire length from Saltville to the Tennessee state line remains impaired for fish consumption (mercury) levels. In this project, one TMDL will be calculated for this entire length for mercury.

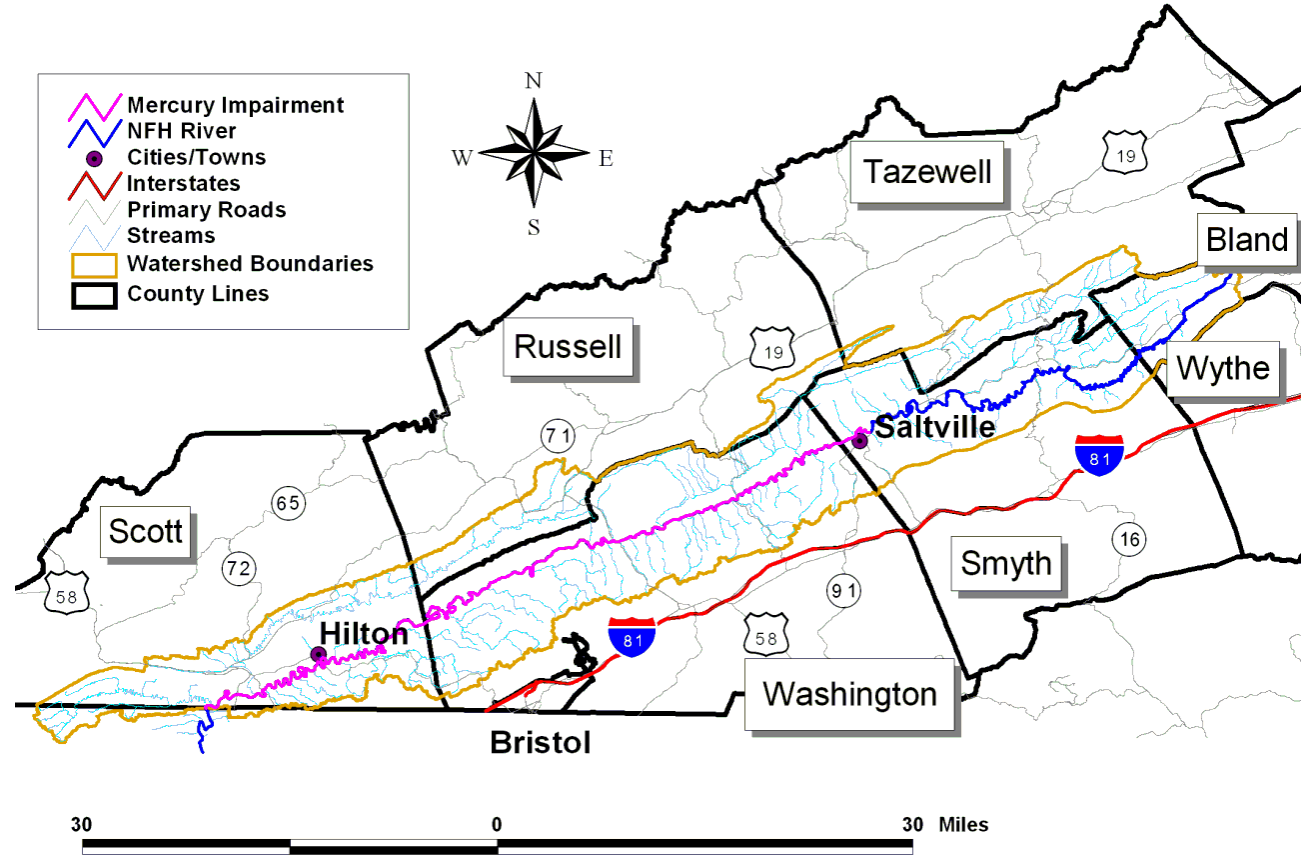


Figure 1.2 The extent of the impairment in the NFHR.

Table 1.1 Fish consumption (Mercury) impairments along the North Fork Holston River.

Stream Name Impairment Id	Impairment(s) Contracted	Initial Listing Year(s)	2006 River Miles	Impairment Location Description
VAS-O10R_NFH01A94	Fish consumption (Mercury)	1996	1.84	Saltville, VA above Olin Plant to Robertson Branch conf.
VAS-O11R_NFH03A94		1996	4.83	Robertson Branch conf. to Tumbling Creek conf.
VAS-O11R_NFH02A94		1996	14.79	Tumbling Creek conf. to Brumley Creek conf.
VAS-O11R_NFH01A00		1996	1.9	Brumley Creek conf. to Cabin Creek conf.
VAS-O12R_NFH02A00		1996	2.82	Cabin Creek conf. to Little Moccasin Creek conf.
VAS-O12R_NFH03C04		1996	8.39	Little Moccasin Creek conf. to Smith Creek conf.
VAS-O12R_NFH02C04		1996	10.76	Smith Creek conf. to Abrams Creek conf.
VAS-O12R_NFH01C02		1996	8.15	Abrams Creek conf. to Livingston Creek conf.
VAS-O12R_NFH01B02		1996	4.25	Livingston Creek conf. to Cove Creek conf.
VAS-O13R_NFH02A94		1996	18.73	Cove Creek conf. to Big Moccasin Creek conf.
VAS-O13R_NFH01A94		1996	5.31	Big Moccasin Creek conf. to TN state line

2. WATER QUALITY ASSESSMENT

2.1 Introduction to Mercury

Mercury is a toxic metal that is released to the environment through natural processes and human-driven activities. Most commonly, the gaseous and particulate forms are released to the atmosphere, which are then deposited onto land and water in precipitation. Once in the water, the mercury can be converted to its most toxic form, methylmercury, which accumulates in fish and aquatic organisms. Humans are exposed to methylmercury and subject to its associated health effects when they consume contaminated fish. In Virginia, fish consumption advisories that have resulted from elevated levels of mercury in certain fish species are of great concern. The vast majority of this mercury can be attributed to atmospheric deposition. The major challenge that the state faces is the lack of available options to control out-of-state sources of atmospheric deposition.

2.1.1 Mercury Speciation and Chemistry

It has long been recognized that the chemical form of mercury (Hg) in air, water, and soil include elemental mercury Hg(0), inorganic ionic mercury (HgII) as soluble (HgIIs) or particulate mercury forms (HgIip), and the organic form called monomethylmercury (MMHg or HgCh₃⁺). Each form has different behaviors that depend on its chemical and physical properties. The predominant source of mercury is atmospheric deposition. The atmospheric burden of mercury arises from both natural and anthropogenic sources accumulated over long periods. Both land and water environments release background mercury in the form Hg(0), except when combustion (forest and other terrestrial fires, fossil fuel combustion, waste combustion, etc.) produces the oxidized form – HgII. Hg(0) dissolves in water according to Henry's Law, and is only weakly soluble in water (about 0.006 ng/l at equilibrium with present-day air concentrations). Thus, Hg(0) must oxidize to HgII, which then is the predominant form of mercury in wet or dry deposition. Hg(0) has a half-life of about 1 year in the atmosphere, while that of HgII varies between hours to months. Only a fraction of mercury entering watersheds from deposition actually is transported into waterbodies. Historically, values ranging from 5 to 50 percent have been reported, and a common value of 25 percent has often been quoted. Most of the mercury

entering the watershed remains in the soil or terrestrial biota, or is reduced to Hg(0) and transfers back to the atmosphere by evasion.

2.1.2 Mercury Transport and Transformations

Mercury that makes its way into aquatic environments is essentially all inorganic ionic HgII. Hg(0) is only weakly soluble in water, while organic forms are usually present in trace amounts with MMHg in the typical range of 0.1 to 5 percent of the total mercury. However, higher amounts of MMHg can enter from wetland drainage. Measurements of MMHg in rainwater seem to be associated with marine production of dimethylmercury, which hydrolyzes to form MMHg. Dimethylmercury does not seem to occur in freshwater environments but only in the marine environment. The ionized forms of mercury (HgII, MMHg) react rapidly and strongly with particulates. Furthermore, ionized forms react strongly with sulfide ions and somewhat strongly with organic complexes. The production of MMHg by microorganisms and its subsequent accumulation in fish is by far the greatest concern. Part of that concern arises from MMHg's long biological half-lives in fish (1-2 years) as opposed to humans and other warm-blooded creatures that have half-lives of 1-3 months. Thus fish can accumulate MMHg to high levels, and the consumed fish – especially long-lived predatory fish – provide exposure of sensitive fish-eating organisms to MMHg.

Two competing processes affect the concentrations of MMHg, methylation produces MMHg while demethylation cleaves the methyl group and then reduces HgII to Hg(0) in a two-step process. The net MMHg produced is what scientists measure and organisms accumulate. Microorganisms perform most of the methylation and demethylation, and sulfate reducing bacteria produce almost all of the MMHg. The concentration of sulfate necessary to support production has an optimum because at higher concentrations, the produced sulfide binds HgII and can make it less available for uptake by sulfate reducing bacteria. Thus, many factors control the production of MMHg: the availability of HgII controlled largely by particulate material and dissolved organic carbon compounds; sulfide and sulfate concentrations; the presence of active sulfate reducing bacteria, and zones of sulfate production. MMHg production is often associated with sediments because most of the HgII is there and anaerobic conditions associated with reductive

processes like sulfate reduction also occur there. The presence of sediments along with a ready source of biodegradable organic carbon resulting from plant production, may explain why wetlands are a major locale for production of MMHg. Circulation with surface waters may make wetland MMHg available for uptake. Emerging insects may substantially increase transfer of MMHg to predatory fish. The food web has an important role in distributing MMHg into fish populations where fish consumers can then become part of the food web. The wide variability in mercury concentrations in similar sized fishes arise from the variety of local conditions of mercury bioavailability, MMHg production, and MMHg transfer among food web components.

2.2 Discussion of In-stream Water Quality - Mercury

VADEQ and Olin Corporation have been collecting water column, fish tissue and sediment data in the North Fork Holston River since 1980.

Comment [FAR1]: Mohammad, Figure 2.1 showing monitoring locations seems to be missing. The current figure 2.1 shows discharge results from Pond 5.

Rod

2.2.1 Water Column Sampling Results

Olin Corporation has been collecting water column total mercury data since 1981. A summary of this data is shown in Table 2.1.

Table 2.1 Average water column total mercury concentrations 1981 – 2004.

River Mile	Description	Mercury Concentration in Water (ng/l)				
		1981-82 Transect ¹ Average	1984-91 Transect ¹ Average	1992-94 Transect ¹ Average	1994-95 Transect ¹ Average	1997-2004 Transect ¹ Average
NFHRM 82.85	Upstream of FCPS near Rt 634 Bridge	5	0	21	2	<5
NFHRM 82.75	Mid point adjacent to FCPS	6	0	15	2	<5
NFHRM 82.65	Downstream of FCPS and railroad bridge	11	0	10	2	<5
NFHRM 82.4	Adjacent to upstream edge of Pond 5	18	4	11	2	<5
NFHRM 81.8	Upstream of Pond 5, previous outfall	25	56	16	13	<5
NFHRM 81.7	Downstream of Pond 5, previous outfall	96	44	78	15	<5
NFHRM 81.5	Downstream of Pond 6 outfall	74	28	53	13	<5
NFHRM 80.8	Adjacent to downstream edge of Pond 6	67	31	43	14	<5
NFHRM 80.0	Former chlorine gas analyzer site	61	27	33	13	<5
NFHRM 77.0	Downstream from intersection of Tumbling Creek Road and North Fork River Road	62	21	22	9	
NFHRM 72.3	Off North Fork River Road	39	21	25	11	

¹ A transect consists of at least two measurements, often three, at the same location (example right bank, middle, left bank), the maximum concentration recorded was 768 ng/L in 1981 at river mile 81.7. Most data presented in this table reflects a time frame that is prior to implementing key remedial activities.

VADEQ has collected water column total mercury data at several monitoring stations between 2000 and 2007. Table 2.2 shows the VADEQ total mercury water column data.

Table 2.2 VADEQ total mercury water column results (August 2000– May 2007).

VADEQ Station_ID	Date	Total Mercury (Ultratrace Method, ng/L)
6CNFH008.78	08/09/00	BDL
6CNFH014.72	03/27/06	1.6
6CNFH033.45	05/13/04	3.25
6CNFH033.45	04/06/05	BDL
6CNFH059.65	08/09/00	BDL
6CNFH067.13	04/05/06	2.5
6CNFH067.13	05/03/07	2.3
6CNFH080.43	07/28/03	8.48
6CNFH089.25	08/09/00	BDL

BDL below minimum detection level.

Olin Corporation collected monthly water column samples from April to September 2008. Samples were analyzed for total mercury as well as dissolved mercury. Samples were collected at 10 locations along the main stem of the NFHR. Results were used in mercury model calibration and bioaccumulation factor (BAF) calculations. Results of this sampling program as presented in Table 2.3 and 2.4.

Table 2.3 Olin Corporation total mercury water column results (April 2008– September 2008).

River Mile	Total Mercury (ng/L)					
	Apr-08	May-08	Jun-08	Jul-08	Aug-08	Sep-08
85	NA	NA	NA	NA	1.0	1.1
84.3	0.83	1.4	0.9	1.1	0.95	1.1
80.1	NA	9.3	6.3	12.2	8.0	7.4
76.9	NA	8.0	6.1	8.1	5.5	10.5
72.3	5.3	7.9	5.4	8.4	6.0	4.7
69.9	4.5	10.0	5.7	16.4	6.1	5.8
60.7	3.6	8.9	7.9	3.9	3.9	5.7
36.2	4.8	5.2	6.1	3.5	2.8	6.0
22.1	4.4	12.0 / 3.3	6.4	14.8	4.4	5.3
8.8	3.8	9.6 / 3.2	7.1	6.3	12.3	6.2

NA Not Analyzed

Table 2.4 Olin Corporation dissolved mercury water column results (April 2008 – September 2008).

River Mile	Total Mercury (ng/L)					
	Apr-08	May-08	Jun-08	Jul-08	Aug-08	Sep-08
85	NA	NA	NA	NA	<0.5	0.78
84.3	<0.5	0.58	<0.12	<0.5	<0.5	0.74
80.1	NA	1.5	3.0	3.3	3.2	3.3
76.9	NA	1.4	2.5	2.6	2.4	3.2
72.3	1.4	1.6	2.1	2.2	2.5	2.6
69.9	1.4	1.3	2.2	2.1	2.2	2.4
60.7	1.3	1.5	2.2	2.0	1.7	2.3
36.2	1.2	NA	2.5	1.6	1.4	2.1
22.1	1.0 J	1.8	2.0	1.7	1.3	1.4
8.8	1.1	1.8	1.8	1.4	1.5	1.4

NA Not Analyzed

2.2.2 Fish Tissue Data Discussion

VADEQ performed fish tissue sampling at four sites in the North Fork Holston River (Table 2.5). These stations are located: at the Rt 23 bridge near Weber City (6CNFH008.80), near Mendota (6CNFH039.18), downstream from Saltville (6CNFH078.55) and near Rich Valley (6CNFH097.67). The VADEQ screening value for mercury in fish tissue is 0.3 mg/Kg while the Virginia Department of Health VDH level of concern (0.5 mg/Kg).

Table 2.5 VADEQ North Fork Holston River fish tissue mercury results

Date	Station	Fish species	Hg, mg/Kg
07/09/97	6CNFH039.18	Northern Hogsucker	0.77
07/09/97	6CNFH039.18	Rock Bass	0.51
07/09/97	6CNFH039.18	Redbreast Sunfish	0.43
07/10/97	6CNFH097.67	Longear Sunfish	0.11
07/10/97	6CNFH097.67	Rock Bass	0.10
07/10/97	6CNFH097.67	Northern Hogsucker	0.09
07/10/97	6CNFH097.67	Redbreast Sunfish	0.07
06/20/02	6CNFH008.80	Rock Bass	0.66
06/20/02	6CNFH008.80	Rock Bass	0.29
06/20/02	6CNFH008.80	Redbreast Sunfish	0.03
06/20/02	6CNFH039.18	Rock Bass	0.58
06/20/02	6CNFH039.18	Redbreast Sunfish	0.45
06/20/02	6CNFH039.18	River Chub	0.39
06/19/02	6CNFH078.55	Smallmouth Bass	0.48
06/19/02	6CNFH078.55	Rock Bass	0.36
06/19/02	6CNFH078.55	Northern Hogsucker	0.11
8/15/2005	6CNFH078.55	Rock Bass	1.31
8/15/2005	6CNFH078.55	Smallmouth Bass	1.23
8/15/2005	6CNFH078.55	Northern Hogsucker	1.22
8/15/2005	6CNFH078.55	Redbreast Sunfish	0.82
8/15/2005	6CNFH078.55	Rock Bass	0.72
8/15/2005	6CNFH078.55	Northern Hogsucker	0.65
8/15/2005	6CNFH078.55	Smallmouth Bass	0.63
8/15/2005	6CNFH078.55	Central Stoneroller	0.13
8/16/2005	6CNFH008.80	Rock Bass	1.09
8/16/2005	6CNFH008.80	Redhorse Sucker	0.76
8/16/2005	6CNFH008.80	Rock Bass	0.72
8/16/2005	6CNFH008.80	Northern Hogsucker	0.68
8/16/2005	6CNFH008.80	Rock Bass	0.63
8/16/2005	6CNFH008.80	Redbreast Sunfish	0.62
8/16/2005	6CNFH008.80	Redbreast Sunfish -	0.57

Table 2.5 VADEQ North Fork Holston River fish tissue mercury results (continued)

Date	Station	Fish species	Hg, mg/Kg
8/16/2005	6CNFH039.18	Smallmouth Bass	2.62
8/16/2005	6CNFH039.18	Northern Hogsucker	1.59
8/16/2005	6CNFH039.18	Redhorse Sucker	1.26
8/16/2005	6CNFH039.18	Northern Hogsucker	1.10
8/16/2005	6CNFH039.18	Rock Bass	1.09
8/16/2005	6CNFH039.18	Northern Hogsucker	1.00
8/16/2005	6CNFH039.18	Rock Bass	0.77
8/16/2005	6CNFH039.18	Redbreast Sunfish	0.74
8/16/2005	6CNFH039.18	Central Stoneroller	0.44
8/16/2005	6CNFH039.18	Redbreast Sunfish	0.24
06/11/07	6CNFH008.80	Rock Bass	0.41
06/11/07	6CNFH008.80	Smallmouth Bass	1.61
06/11/07	6CNFH008.80	Smallmouth Bass	0.80
06/14/07	6CNFH039.18	Redbreast Sunfish	0.91
06/14/07	6CNFH039.18	Rock Bass	0.87
06/14/07	6CNFH039.18	Smallmouth Bass	1.91
06/14/07	6CNFH039.18	Smallmouth Bass	1.65
06/14/07	6CNFH078.55	Smallmouth Bass	1.45

Bold values exceed the VADEQ screening value of 0.3 mg/Kg

The results of this monitoring show the majority of samples (82%) exceed the VADEQ screening criteria of 0.3 mg/Kg. The exceptions were primarily samples collected upstream of Saltville at Rich Valley. The different species of fish tissue samples collected include: Northern Hogsucker, Rock Bass, Smallmouth Bass, Redbreast Sunfish, Redhorse Sucker, River Chub, Longear Sunfish and Stoneroller. The VDH level of concern (0.5 mg/Kg) was exceeded in 62% of the 49 samples.

Olin Corporation has been analyzing mercury fish tissue data since 1981. Samples have been collected from 24 different locations and from 19 different fish species. Table 2.6 and Figure 2.1 show the maximum annual mercury tissue concentration from Rock Bass collected at the six long-term monitoring sites (1981 – 2005) on the North Fork Holston River. The VADEQ screening value of 0.3 mg/Kg was exceeded in 96% of the Rock Bass samples shown in Table 2.5 and the Virginia Department of Health VDH level of concern (0.5 mg/Kg) was exceeded in 84%.

Table 2.6 Olin Corporation North Fork Holston River Rock Bass maximum annual fish tissue mercury results (mg/kg).

Year	River Mile					
	NFHR 8 (mg/kg)	NFHR 22 (mg/kg)	NFHR 36 (mg/kg)	NFHR 72 (mg/kg)	NFHR 77 (mg/kg)	NFHR 98 (mg/kg)
1981	1.44	2.07	3.13	1.92	3.82	0.54
1982	1.09	2.15	1.70	2.26	2.49	0.46
1983	1.17	1.86	1.75	2.19	2.68	0.40
1984	1.66	2.02	1.95	1.96	3.21	1.14
1985	1.23	1.48	1.63	2.00	2.16	0.65
1986	1.53	1.64	1.71	1.86	2.46	0.43
1987	1.21	1.97	1.82	1.87	2.25	0.46
1988	1.23	2.25	1.86	1.66	1.79	0.51
1989	1.50	1.50	1.50	1.80	1.60	0.40
1990	1.40	1.60	1.40	1.60	2.40	0.30
1991	1.20	1.40	1.50	2.00	1.70	0.50
1992	1.27	1.39	1.53	2.07	1.63	0.32
1993	1.10	1.30	1.50	1.50	1.40	0.45
1994	0.93	1.20	1.20	2.10	1.80	0.49
1995	0.93	1.20	1.50	1.80	1.10	0.24
1996	1.32	1.55	1.72	1.69	1.05	0.33
1997	0.55	0.96	1.73	1.70	1.83	0.32
1998	0.10	1.39	1.35	1.05	0.86	0.29
1999	0.47	1.39	1.34	0.88	1.87	1.22
2000	0.15	0.35	0.41	0.79	0.74	0.76
2001	0.35	0.77		1.13	0.84	0.22
2002	1.42	0.92	1.07	0.98	0.95	0.88
2003	0.74	1.05	0.50	0.81	1.00	0.64
2004	0.35	0.97	1.23	1.62	0.78	
2005	0.77	0.81	1.00	2.30	1.10	1.40

Bold values exceed the VADEQ screening value of 0.3 mg/Kg, river mile 8 is the most downstream location and is located near Weber City and river mile 98 is located near Rich Valley.

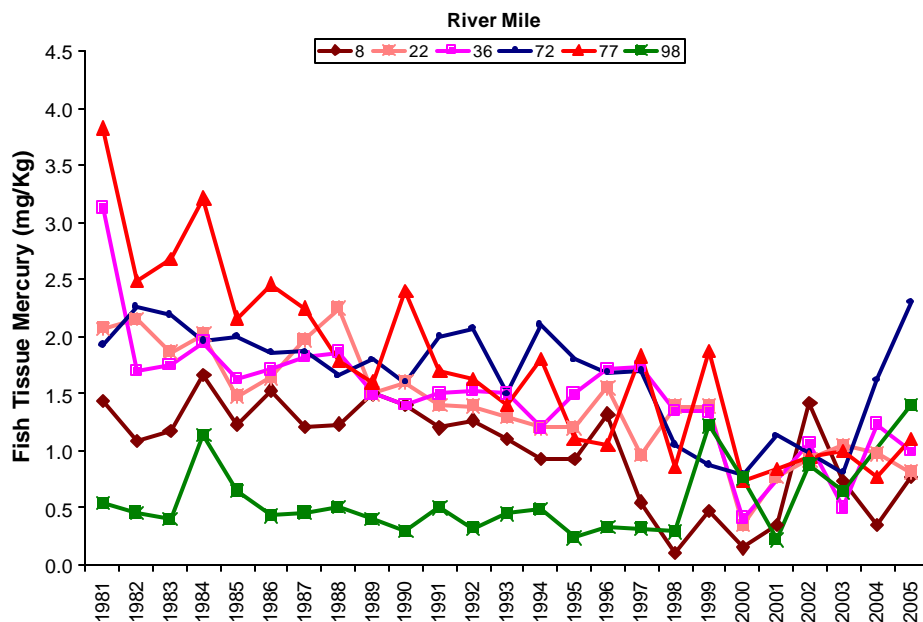


Figure 2.1 Olin Corporation North Fork Holston River Rock Bass fish tissue maximum annual mercury results

2.2.3 Sediment Sampling Results

VADEQ performed sediment sampling at 14 sites on the North Fork Holston River from 1980 to 2005. Table 2.7 shows the results of these sampling efforts organized by station from downstream to upstream and by year for each station. Fifty-nine percent of the samples were higher than the consensus probable effect (PEC) screening value of 1.060 mg/Kg. All of the sediment samples that exceeded the screening value were collected at and downstream of Saltville. Additional data reflecting more recent sampling results will be included in the final version of this report.

Table 2.7 Streambed sediment mercury results from VADEQ monitoring.

Station	Date	Hg (mg/Kg)	Station Type
6CNFH008.78	05/20/80	1.32	Ambient
6CNFH008.78	06/10/81	0.34	Ambient
6CNFH008.78	06/21/83	0.30	Ambient
6CNFH008.78	04/04/85	1.48	Ambient
6CNFH008.78	03/20/86	1.30	Ambient
6CNFH008.78	03/17/87	0.82	Ambient
6CNFH008.78	03/16/89	0.20	Ambient
6CNFH008.78	03/20/90	0.20	Ambient
6CNFH008.78	03/18/91	1.20	Ambient
6CNFH008.78	08/16/95	0.48	Ambient
6CNFH008.78	05/20/97	0.75	Ambient
6CNFH008.80	06/20/02	0.50	FT&Sediment
6CNFH008.80	06/20/02	0.48	FT&Sediment
6CNFH008.80	8/16/2005	0.02	FT&Sediment
6CNFH014.72	03/27/06	1.00	Ambient
6CNFH020.93	03/17/03	0.56	Ambient
6CNFH033.45	05/13/04	0.25	Ambient
6CNFH033.45	04/06/05	0.86	Ambient
6CNFH039.18	05/20/80	2.62	Ambient
6CNFH039.18	06/10/81	2.80	Ambient
6CNFH039.18	06/21/83	1.44	Ambient
6CNFH039.18	04/04/85	2.00	Ambient
6CNFH039.18	03/17/87	1.86	Ambient
6CNFH039.18	03/16/89	1.00	Ambient
6CNFH039.18	03/20/90	1.70	Ambient
6CNFH039.18	04/29/91	0.70	Ambient
6CNFH039.18	07/09/97	2.90	FT&Sediment
6CNFH039.18	06/20/02	1.36	FT&Sediment
6CNFH039.18	8/16/2005	0.59	FT&Sediment
6CNFH047.64	05/08/02	0.87	Ambient

Bold values are above the PEC value for mercury in sediment = 1.06 mg/Kg

Ambient stations are routine VADEQ monitoring stations, FT&Sediment are special study fish tissue and sediment monitoring stations. Special study data is analyzed at the Virginia Institute of Marine Science Laboratory.

Table 2.7 Streambed sediment mercury results from VADEQ monitoring (continued).

Station	Date	Hg (mg/Kg)	Station Type
6CNFH059.65	05/20/80	0.41	Ambient
6CNFH059.65	06/10/81	4.50	Ambient
6CNFH059.65	06/21/83	1.72	Ambient
6CNFH059.65	04/04/85	4.60	Ambient
6CNFH059.65	03/20/86	2.20	Ambient
6CNFH059.65	03/17/87	1.63	Ambient
6CNFH059.65	03/16/89	2.90	Ambient
6CNFH059.65	03/20/90	5.40	Ambient
6CNFH059.65	04/29/91	1.20	Ambient
6CNFH059.65	07/22/92	1.30	Ambient
6CNFH059.65	12/05/95	5.60	Ambient
6CNFH059.65	05/20/97	1.54	Ambient
6CNFH059.65	06/03/99	1.52	Ambient
6CNFH067.13	04/05/06	1.93	Ambient
6CNFH067.13	05/03/07	1.97	Ambient
6CNFH078.55	06/19/02	1.11	FT&Sediment
6CNFH078.55	8/15/2005	0.57	FT&Sediment
6CNFH080.43	05/15/80	5.20	Ambient
6CNFH080.43	06/24/81	7.60	Ambient
6CNFH080.43	06/15/83	29.00	Ambient
6CNFH080.43	07/19/84	0.16	Ambient
6CNFH080.43	03/19/86	7.10	Ambient
6CNFH080.43	03/10/87	5.90	Ambient
6CNFH080.43	03/15/89	3.00	Ambient
6CNFH080.43	03/28/90	7.36	Ambient
6CNFH080.43	04/03/91	3.30	Ambient
6CNFH080.43	07/30/91	2.40	Ambient
6CNFH080.43	07/13/92	4.00	Ambient
6CNFH080.43	10/20/94	3.46	Ambient
6CNFH080.43	07/02/96	2.00	Ambient
6CNFH080.43	05/20/97	2.00	Ambient
6CNFH080.43	06/03/99	1.88	Ambient
6CNFH080.43	07/28/03	2.42	Ambient
6CNFH083.32	06/15/83	1.72	Ambient
6CNFH083.32	07/19/84	1.19	Ambient
6CNFH083.32	03/19/86	5.10	Ambient
6CNFH083.32	03/15/89	0.90	Ambient
6CNFH083.32	03/28/90	1.30	Ambient
6CNFH083.32	04/03/91	2.80	Ambient

Bold values are above the PEC value for mercury in sediment = 1.06 mg/Kg

Ambient stations are routine VADEQ monitoring stations, FT&Sediment are special study fish tissue and sediment monitoring stations. Special study data is analyzed at the Virginia Institute of Marine Science Laboratory.

Table 2.7 Streambed sediment mercury results from VADEQ monitoring (continued).

Station	Date	Hg (mg/Kg)	Station Type
6CNFH083.94	05/02/02	0.42	Ambient
6CNFH085.20	05/15/80	0.10	Ambient
6CNFH085.20	06/24/81	0.04	Ambient
6CNFH085.20	06/15/83	0.24	Ambient
6CNFH085.20	03/19/86	0.22	Ambient
6CNFH085.20	03/10/87	0.12	Ambient
6CNFH097.67	06/24/81	0.38	Ambient
6CNFH097.67	03/19/86	0.06	Ambient
6CNFH097.67	03/15/89	0.20	Ambient
6CNFH097.67	07/10/97	0.17	FT&Sediment

Bold values are above the PEC value for mercury in sediment = 1.06 mg/Kg

Ambient stations are routine VADEQ monitoring stations, FT&Sediment are special study fish tissue and sediment monitoring stations. Special study data is analyzed at the Virginia Institute of Marine Science Laboratory.

2.2.4 Ground Water Sampling Results

Olin Corporation monitored ground water in the vicinity of ponds 5 and 6 between March 2003 and November 2006. Data were collected from 24 different monitoring sites. Seventy Five percent of the values were below the minimum laboratory detection level. A summary of the data is provided in Table 2.8. A more detailed dataset will be presented in the final version of this draft report.

Table 2.8 Olin Corporation total mercury ground water monitoring results.

Date	Count	Minimum	Maximum	Mean	Median	Standard Deviation
03/2003 – 11/2006	122	0.09	162	4.09	0.83	15.47

Total mercury values are in ug/L.

2.3 Mercury Standards

The General Standard and the Designated Uses standard state that surface waters should be free of pollutants that affect the health of humans, animals, and aquatic life, while maintaining the six designated uses.

The VADEQ standards for mercury in surface waters (freshwater) are shown in Table 2.9.

Table 2.9 Virginia Water Quality Standards for Mercury in Fresh Surface Water

Aquatic Life		Human Health	
Acute	Chronic	Acute	Chronic
1.4	0.77	0.05	0.051

All values are in ug/L (micro grams per liter or parts per billion (ppb)).

Mercury is more likely to be found in streambed sediments and in fish tissues within a contaminated channel. Because of this, VADEQ also monitors streambed sediment and fish tissue. The VADEQ mercury sediment screening value is 1.060 ppm and the fish tissue screening value is 0.3 ppm. The VADEQ will list a stream as impaired for not supporting the fish consumption use when 1) two or more fish tissue samples from different species exceed the screening value during a single sampling event, or 2) if two or more samples of the same or different fish species exceed the screening value in two or more monitoring events, or 3) if there is a VDH fish consumption advisory or ban due to high mercury (note the VDH mercury level of concern is 0.5 ppm).

The Virginia Department of Health (VDH) is responsible for issuing and publicizing fish consumption bans and advisories. The VDH takes VADEQ water column, sediment, and fish tissue data and further analyzes the amount of recreational fishing and fish consumption by local citizens, among other factors. VDH can issue a limited fish consumption advisory or a “Do not eat” consumption ban depending on the severity of the contamination. The North Fork Holston River main stem is under a (VDH) fish consumption ban due to mercury contamination from Saltville to the Virginia/Tennessee state line (approximately 82 stream miles). The ban has been in effect since the 1970s.

2.4 Site-Specific Endpoint

The VA DEQ developed a site-specific endpoint for the NFHR mercury impairment. The study involved analyzing fish tissue data from several locations along the main stem of the river. Bioaccumulation factor (BAF) was developed for the NFHR based on smallmouth bass fish tissue. Smallmouth bass was selected since it is the highest trophic level consumer in the NFHR.

The BAF is calculated as the ratio of mercury in fish tissue at a given location to mercury concentration in water body (water column concentration) as shown in the equation below:

$$\text{BAF (L/kg)} = F / C_{aw}$$

where:

F is the fish tissue mercury concentration (mg/kg)

C_{aw} is the ambient mercury concentration in water column (mg/L)

The median smallmouth bass tissue concentration of 1.4 mg/kg at river mile 60 was used in the BAF calculations. The water column concentration used was 7.5 ng/L which was measured as the average concentration of THg between river miles 60.7 and 80.1 during the 2008 sampling. These concentrations resulted in a BAF of 186,667 L/kg.

A site-specific water column endpoint was then be obtained by dividing the fish advisory criterion by the BAF as follows:

$$C_s = C_r / \text{BAF}$$

where:

C_s is the site-specific water column endpoint

C_r is the fish advisory criterion

Based on this formula, the site-specific endpoint is estimated as 0.3 mg/kg divided by 186,667 L/kg, which is approximately 2 ng/L.

3. SOURCE ASSESSMENT

As part of the TMDL development process, known sources of mercury in the watershed were identified and quantified. Non-point and point sources were included in the analysis.

3.1 Known Mercury Sources

Mercury is found in the environment from both natural and manmade sources. The largest source of total mercury is from coal-fired power plants. Other sources of mercury include chlor-alkali plants that use mercury to convert salt to chlorine gas and caustic soda (lye). Most of the existing chlor-alkali plants are converting to a cleaner process that doesn't require mercury. Auto scrap yards can also be significant sources of mercury and in 2003 US automakers stopped using mercury in the manufacturing of automobiles. Mercury is still used in the production of PVC pipe, traditional medicines, electrical switches, batteries and dental amalgam. It is naturally occurring in geologic formations and in volcanoes. In some parts of the world it is still used in the process of gold mining (<http://www.NRDC.org/health/effects/mercury/sources.asp>), accessed January 27, 2009.

Both point and nonpoint sources are represented in the study. In general, point sources are incorporated as time-series of pollutant and flow inputs to the stream at the proper location. Land-based nonpoint sources are represented as sediment-bound mercury which gets washed off to the streams during rainfall events. This activity occurs within the contaminated floodplain areas as well as the upland areas that are only impacted by atmospheric deposition. The mercury input from atmospheric deposition as well as interflow and groundwater are considered.

3.2 Known Mercury Contaminated Site

A Superfund site exists in Saltville and carries EPA permit number VAD003127578. The former Olin Mathison Chlor Alkali Plant operated from 1950 to 1972 and produced chlorine and caustic soda (lye). The production process required the mining of salt and the use of mercury. Olin constructed a treatment plant to treat the effluent from Pond 5 in 1994. Figure 3.1 shows mercury measurements from the treated water discharged to

North Fork Holston. A more complete dataset will be presented in the final version of the report. Figure 3.2 shows the location of the discharge to the North Fork Holston.

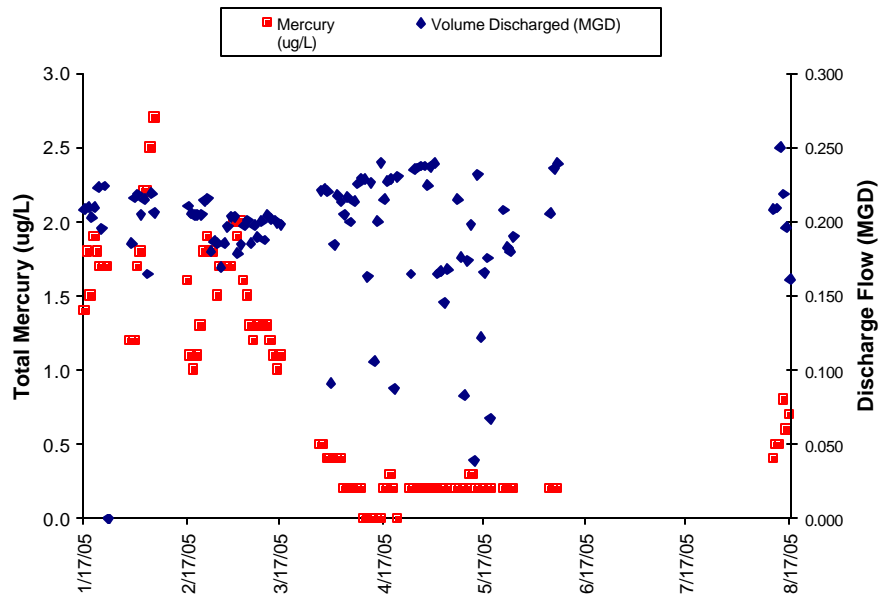


Figure 3.1 Total mercury discharged from the treatment facility at Pond 5.



Figure 3.2 Location of Olin superfund treatment plant discharge to the North Fork Holston River.

3.3 VADEQ Permitted Facilities in the North Fork Holston River Drainage Area.

VADEQ has issued permits for 54 facilities in the North Fork Holston River drainage area. They consist of one carwash, 10 VPDES, five mining, 37 domestic and one industrial stormwater permit. None of these facilities currently has permit discharge limits for mercury. Table 3.1 lists the permits by type.

Out of the many point sources available within the drainage area under study, three were considered in the analysis due to their relatively high design flow. The three permitted point sources were Scott County PSA - Holston Regional WWTP with a design flow of 1.25 MGD; Saltville Town – WWTP with a design flow of 0.99 MGD; and Texas Brine Company - Saltville LLC with a design flow of 0.575 MGD. The actual monitored data

were used in the calibration of the model while the design flow capacity was used during allocation runs. These point sources did not hold a permit to discharge mercury and mercury is not currently required as a monthly sampling parameter. However, based on a single sampling event, the concentration of mercury with the outflow of these point sources was assigned a value of one nanogram per liter (ng/L).

Table 3.1 VADEQ VPDES permitted facilities in the drainage area.

Permit	Type	Name	Location	Permitted Flow, MGD	Receiving Stream
VAG750006	Carwash	Pine Ridge Car Wash	Hwy 58 two mi. west of Hiltons, VA	0.0005	UT NFH River
VAG400333	Domestic	Heritage Baptist Church	US 421/58	0.0010	NFH ,UT
VAG400223	Domestic	1st Baptist Church of Lime Hill Road	20353 Lime Hill Road	0.0010	Abrams Creek, UT
VAG400225	Domestic	Residential	Rte 3 Box 332B	0.0010	Poor Valley Branch
VAG400244	Domestic	Residential	Route 3 Box 555	0.0010	Poor Valley Branch
VAG400251	Domestic	Residential	Route 4 Box 397M	0.0010	NFH River, UT
VAG400011	Domestic	Residential	Route 6 Box 245	0.0010	Little Moccasin Creek
VAG400013	Domestic	Barnette Enterprises STP	330 Wadlow Gap Rd	0.0010	Henderson Branch, UT
VAG400017	Domestic	Residential	Rte 3 Box 608C	0.0010	Possum Creek, UT
VAG400082	Domestic	Residential	Route 1 Box 23C10	0.0010	Hilton Creek, UT
VAG400086	Domestic	Residential	30134 Aistrop Rd	0.0010	Count Br, UT
VAG400088	Domestic	Greendale Chapel Fellowship Hall STP	Route 700	0.0010	Greendale Creek
VAG400028	Domestic	Residential	Route 6	0.0010	Little Moccasin Creek
VAG400042	Domestic	Residential	30095 North Fork River Road	0.0010	NFH River
VAG400045	Domestic	Residential	18393 McCalls Gap Road	0.0010	Livingston Creek
VAG400057	Domestic	Residential	Route 4 Box 411-C	0.0010	NFH River, UT
VAG400061	Domestic	Residential	Route 7, Box 1524	0.0010	Possum Creek, UT
VAG400150	Domestic	Lane Company Incorporated - Gate City	Rte 4 Box 358-Q	0.0010	NFH, UT
VAG400161	Domestic	Residential	Route 4 Box 437R	0.0010	NFH, UT
VAG400172	Domestic	Residential	Route 4 Box 358T	0.0010	NFH River, UT

NA – There is no permitted flow for industrial stormwater and mining permits., UT - Unnamed Tributary

Table 3.1 VADEQ VPDES permitted facilities in the drainage area (cont).

Permit	Type	Name	Location	Permitted Flow, MGD	Receiving Stream
VAG400145	Domestic	Residential	109 Stagecoach Ln	0.0010	Watson Gap Branch, UT
VAG400103	Domestic	Residential	15045 Fall Hill Road	0.0010	Falls Hill Creek
VAG400119	Domestic	Residential	Rte 4 Box 498-C	0.0010	NFH River
VAG400124	Domestic	Little Flock Holiness Church STP	8417 Old Mill Road	0.0010	Keywood Branch
VAG400572	Domestic	Hilton Commercial Strip Mall STP	Intersection of US 58 and St Rte 709	0.0010	Hilton Creek
VAG400066	Domestic	Residential	3088 Willow Branch Road	0.0010	Williow Branch
VAG400607	Domestic	Residential	US 58/421	0.0010	NFH River, UT
VAG400623	Domestic	Residential	St Rt 637	0.0010	Possum Creek
VAG400520	Domestic	Valley Chapel and Parsonage STP	ST Rt 689	0.0010	Brumley Creek, UT
VAG400693	Domestic	Residential	St Rt 614	0.0010	Poor Valley Branch
VAG400599	Domestic	Residential	St Rte 614	0.0010	Poor Valley Branch, UT
VAG400527	Domestic	Residential	32214 and 32222 Old Salt Works Rd	0.0010	Stonemill Creek
VAG400687	Domestic	Residential	St Rt 687	0.0010	NFH River
VAG400481	Domestic	Residential	9395 Old Mill Rd	0.0010	Keywood Branch
VAG400582	Domestic	Residential	14705 Yuma Rd	0.0010	Poor Valley Branch
VAG400584	Domestic	Residential	St Rte 713 Stanley Valley	0.0010	Stanley Valley Creek
VAG400732	Domestic	Residential	US 19	0.0010	Greendale Creek

NA – There is no permitted flow for industrial stormwater and mining permits., UT - Unnamed Tributary

Table 3.1 VADEQ VPDES permitted facilities in the drainage area (cont).

Permit	Type	Name	Location	Permitted Flow (MGD)	Receiving Stream
VAG400366	Domestic	Rally Mart 1	Intersection of US 58 and St Rt 709	0.0010	Hilton Creek
VAR050120	Ind Stormwater	Titan Wheel Corporation of Virginia	227 Allison Gap Road Saltville, VA	NA	NFH River
VAG840013	Mining	Vulcan Construction Materials - Speers Ferry Quarry	Rte 1 Box 252A Gate City, VA	NA	Troublesome Creek
VAG840020	Mining	General Shale Products LLC - Yuma Mine 18	Rte 3 Yuma Rd Gate City, VA	NA	Jones Branch
VAG840198	Mining	General Shale Brick - McMurray Mine	St Rte 693 Gate City, VA	NA	Hensley Hollow
VAG840199	Mining	General Shale Brick - McMurray Mine	St Rte 693 Gate City, VA	NA	Fowler Branch
VAG840200	Mining	General Shale Brick - McMurray Mine	St Rte 693 Gate City, VA	NA	Fowler Branch, UT
VA0021083	VPDES	Scott County Public Schools - Hilton Elementary	St Rt 709	0.0040	Hilton Creek
VA0026786	VPDES	Washington County Public Schools - Valley Institute	4350 Gate City Highway	0.0060	Fleenor Branch
VA0026808	VPDES	Saltville Town - WWTP	336 Allison Gap Road	0.9900	NFH River
VA0029084	VPDES	Bellamys Repair Shop STP	Rt 58	0.0050	Hiltons Creek
VA0029688	VPDES	Smyth County Public Schools - Northwood Middle	156 Longhollow Road	0.0093	NFH River
VA0063673	VPDES	Washington Cnty Public Schools - Greendale Elem	13092 McGuffie Drive/Route 700, 0.5 Mile From Intersection w/ Rte 19	0.0132	Canoe Branch
VA0064033	VPDES	Scott County Public Schools - Yuma Elementary STP	Intersection of St Rts 614 and Route 866	0.0050	Cate Branch
VA0067351	VPDES	Scott County PSA - Holston Regional WWTP	Miller Road	1.2500	NFH River
VA0078531	VPDES	Pine Ridge Trailer Park STP	US 58, 2 miles West of Hiltons	0.0050	NFH River, UT
VA0090115	VPDES	Texas Brine Company - Saltville LLC	889 Ader Lane	0.5750	McHenry Creek

NA – There is no permitted flow for industrial stormwater and mining permits., UT - Unnamed Tributary

3.4 Nonpoint Sources

The nonpoint sources of mercury in the NFHR watershed include atmospheric deposition on river reaches, mercury in interflow and groundwater, and mercury attached to top soil within the contaminated floodplain area as well as background areas that reaches streams via runoff during storm events. The concentrations were either used as measured in the field or were adjusted during the model calibration process. Table 3.2 summarizes these sources along with estimation method and utilized concentrations.

Table 3.2 Nonpoint sources within NFHR watershed as used in modeling procedures.

Nonpoint Source	Estimation Method	Concentrations used in model
Atmospheric deposition	EPA Mercury atmospheric deposition network, varied by month	13.6 to 30.4 ng/L
Groundwater from upland areas	Same as concentration observed upstream of contaminated site	1 ng/L
Groundwater within contaminated floodplain areas	Between background and middle of atmospheric deposition	1 ng/L to 10 ng/L
Hg attached to sediment with runoff from non-contaminated areas	Background concentration measured with floodplain upstream of site	0.11 mg/kg
Hg attached to sediment with runoff from contaminated areas	Measured concentrations in top 6 inches using median of field measurements concentrations	0.12 to 2.3 mg/kg

4. MODELING PROCEDURE: LINKING THE SOURCES TO THE ENDPOINT

Computer modeling is used in this study as a tool that allows simulating the interaction between the land surface and subsurface and the quantities of various mercury sources by location. The model allows the climatological factors and in particular, precipitation, to drive this interaction. By modeling the watershed conditions and mercury sources, the model allows quantifying the relationship between sources as they exist throughout the watershed to mercury concentration within the river itself. The model used in the analysis was the USGS Hydrologic Simulation Program - Fortran (HSPF) water quality model. The HSPF model is a continuous simulation model that can account for NPS pollutants in runoff, as well as pollutants entering the flow channel from point sources.

Since mercury transport is driven by the flow of water and movement of sediment, two components of the model had to be built first, dealing with flow and sediment (or total suspended solids, TSS) movement. The flow component was calibrated by comparing model output to observed flow within the NFHR and making the proper adjustments to obtain the best match between simulated and observed flow. Once the flow component was built, the sediment component was constructed and calibrated by comparing model simulations of sediment to observed TSS values collected by DEQ at various locations. The third and final component of the model was the mercury transport component, which utilizes the first two components. The mercury transport component of the model was calibrated by comparing model simulations to observed water column concentrations collected in 2008. The accuracy of all three components was assessed and deemed satisfactory by the TMDL working group.

In the mercury component of the model, mercury loadings from various sources are simulated including point sources, FCPS sources, runoff from both contaminated floodplain and background areas, interflow and groundwater, and direct atmospheric deposition on water surface. Once mercury reaches the river, the model simulates relevant processes that impact concentration of mercury in water column and sediment. These processes include mercury sorption to suspended particles and desorption from these particles, sediment deposition and resuspension, and downstream advection. Complete description of the modeling approach is presented in Appendix B.

The modeling approach followed in this study is similar in nature to the one used previously in the Commonwealth of Virginia to address mercury contamination issues. In specific, the approach followed here was similar to the one adopted for the South River, South Fork Shenandoah River, and Shenandoah River mercury TMDL conducted by the USGS. A parallel modeling effort was also conducted by MACTEC. The results of both modeling approaches were compared for all stages of the process. Both modeling efforts were deemed comparable with similar intermediate (flow and sediment) and end results (mercury).

5. ALLOCATION

Total Maximum Daily Loads (TMDLs) consist of waste load allocations (WLAs, permitted sources) and load allocations (LAs, nonpoint sources) including natural background levels. Additionally, the TMDL must include a margin of safety (MOS) that either implicitly or explicitly accounts for the uncertainties in the process (*e.g.*, accuracy of source assessment). The definition is typically denoted by the expression:

$$\text{TMDL} = \text{WLAs} + \text{LAs} + \text{MOS}$$

The TMDL becomes the amount of a pollutant that can be assimilated by the receiving waterbody and still achieve water quality standards. For the current project, the TMDL is expressed in terms of grams per year.

5.1 Existing Conditions

Once the model was calibrated for hydrology, sediment, and mercury, the model was used to simulate the existing conditions in the watershed. Existing conditions were obtained as a result of measurements in the field, information obtained about point sources as well as the results of mercury calibration. The simulation period used for estimating the existing conditions was the same period used for mercury calibration and hydrologic validation. Mercury concentration representing existing conditions is shown in Figure 5.1.

The majority of mercury loading (95%) enters the river with sediment during runoff events from both contaminated floodplain areas and background areas. Mercury loading via interflow accounts for approximately 2%. Direct contribution of FCPS sources is approximately 1% with groundwater contributing approximately the same amount. Direct atmospheric deposition on water surfaces and point sources contribute approximately 0.1% each. Figure 5.2 shows the relative contribution of all sources at existing conditions.

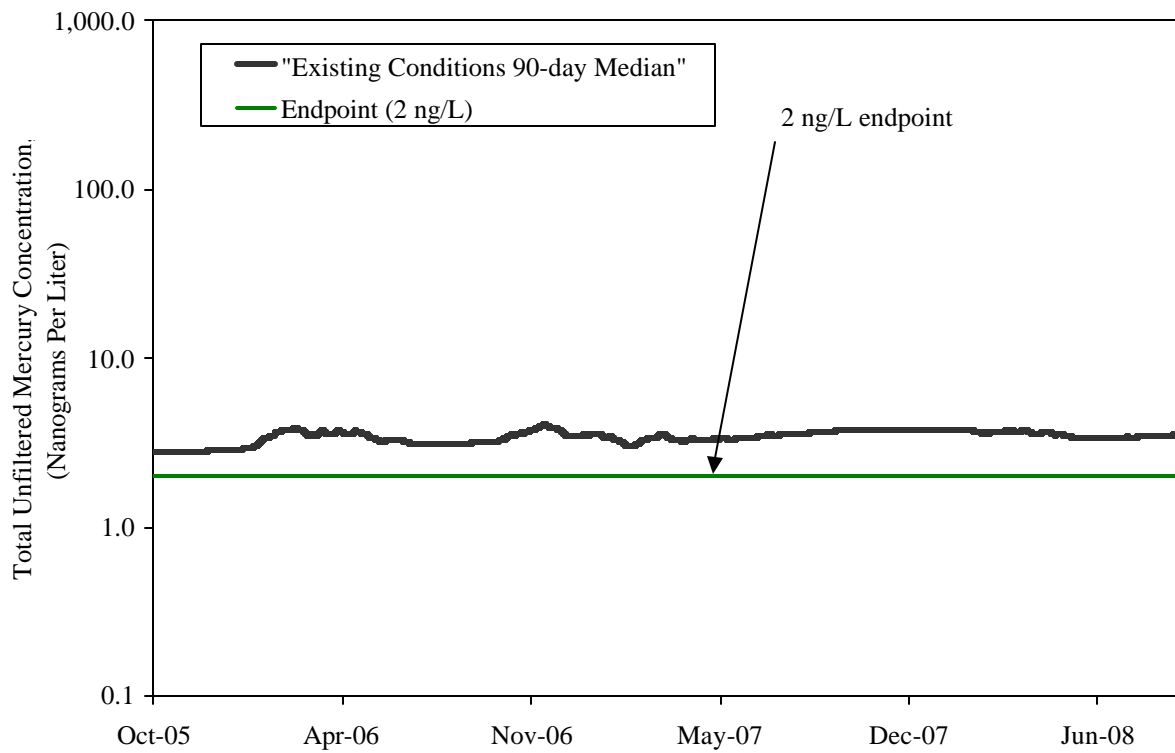


Figure 5.1 Model simulation of mercury concentration under existing conditions.

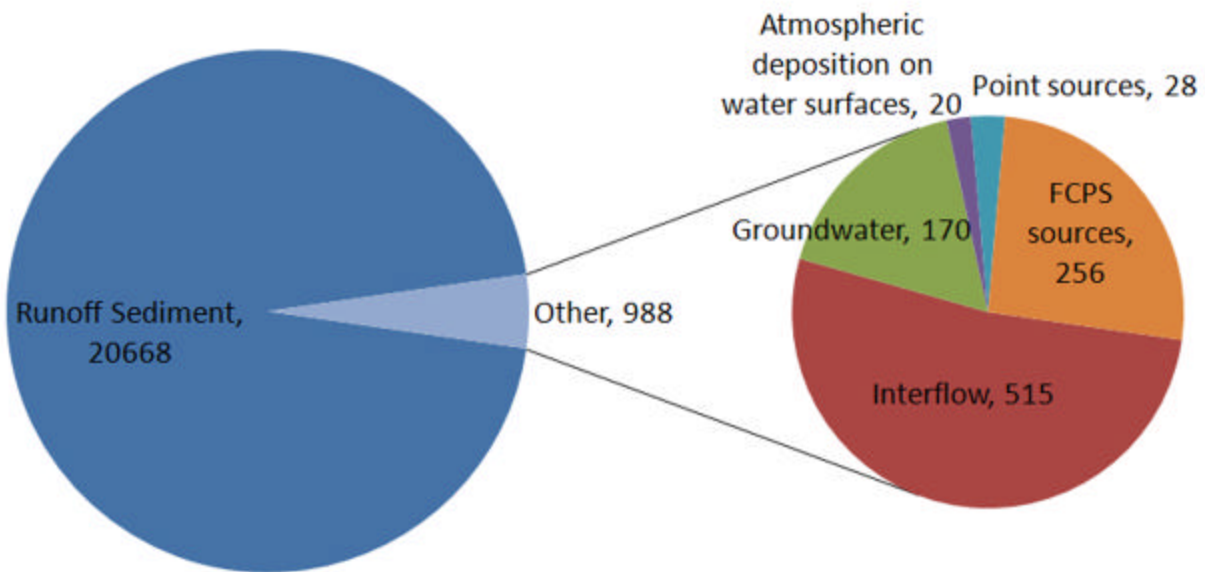


Figure 5.2 Source contribution of mercury under existing conditions in grams per year.

5.2 Incorporation of a Margin of Safety

In order to account for uncertainty in modeled output, a MOS was incorporated into the TMDL development process. Individual errors in model inputs, such as data used for developing model parameters or data used for calibration, may affect the load allocations in a positive or a negative way. A margin of safety can be incorporated implicitly in the model through the use of conservative estimates of model parameters, or explicitly as an additional load reduction requirement. The intention of an MOS in the development of this mercury TMDL is to ensure that the modeled loads do not underestimate the actual loadings that exist in the watershed.

An implicit MOS was used in the development of this TMDL. By adopting an implicit MOS in estimating the loads in the watershed, it is ensured that the recommended reductions will in fact succeed in meeting the water quality standard. Examples of the implicit MOS used in the development of this TMDL are:

- Allocating permitted point sources at the endpoint value of 2 ng/L and at maximum permitted flow rate, and
- Selecting a modeling period that represented the critical hydrologic conditions in the watershed, and
- Ensuring that the model simulated output concentration has a range of values that includes and exceeds the highest sampled concentration at least part of the time, and
- Basing the bioaccumulation factor on the smallmouth bass which is the highest trophic level consumer in the NFHR.

5.3 Scenario Development

Using mercury loads representing existing conditions as model inputs, reductions were applied to those loads until the endpoint was met. The mercury TMDL developed for the NFHR was based on the 90-day median of the total unfiltered mercury staying below the 2 ng/L endpoint.

Pollutant concentrations were modeled over the entire duration of a representative modeling period and pollutant loads were adjusted until the goal was met (Figure 5.1). The development of the allocation scenario was an iterative process that required

numerous runs with each followed by an assessment of source reduction against the water quality target.

5.3.1 Waste Load Allocations

The allocation for the three main point sources is equivalent to their current permit levels design flow with a concentration of total unfiltered mercury of 2 ng/L.

5.3.2 Load Allocations

Load allocations to nonpoint sources are divided into land-based loadings from land uses and sources related to the FCPS. Source reductions include those that are affected by both high and low flow conditions. Land-based NPS loads had their most significant impact during high-flow conditions, while sources related to the FCPS tend to act similar to point sources and have their most significant impact on low flow concentrations.

Allocation scenarios were run with sequential reductions until there was 0% exceedance of the endpoint at the outlet of the NFHR at the state line. Table 5.1 represents a portion of the scenarios developed to determine the TMDL. The first row in the table shows the baseline scenario with existing conditions. At existing conditions, and according to computer simulations, the 90-day median is expected to always be above the target endpoint of 2 ng/L.

Scenario 1 shows the expected impact of reducing the mercury influx with runoff sediment by 80%. This scenario results in a lower 90-day median and a lower percent of the time the 2 ng/L endpoint is exceeded. In Scenario 2, mercury in atmospheric deposition is reduced by 20% which is also assumed to reduce mercury in interflow by a similar amount. This reduction lowers the 90-day median and percent of time the 2 ng/L endpoint is exceeded even further. In Scenarios 3 through 5 examine the impact of reducing the influx of mercury from point sources as well as sources related to the FCPS by various amounts. While Scenarios 3 through 5 all meet the endpoint, Scenario 5 is favored since it allows for the least reduction while still meeting the endpoint.

Scenario 6 shows the expected results if fewer reductions were recommended from mercury in sediment and more reductions to point sources and FCPS related sources.

This scenario failed to meet the endpoint all the time. The endpoint was met if reductions to mercury in sediment were increased from 50% to 70% as in Scenario 7. Scenario 8 explores the case of having minimum reductions to point sources and FCPS related sources with a higher reduction to mercury in sediment. This approach required a high (90%) reduction in mercury with runoff to meet the endpoint all the time. Scenario 9 shows what the percentage reduction would be if equal reductions were recommended from mercury in runoff as well as point sources and FCPS related sources. The expected reduction is 72%.

Finally, Scenario 10 examines the impact of reducing influx of mercury with groundwater by half the reduction to atmospheric deposition and interflow. Such reduction in groundwater contribution may be expected years down the road depending on the lag time in the watershed that it takes for changes on the surface of the ground to be reflected in groundwater. With a 10% reduction to groundwater contribution of mercury, less reductions in point sources and FCPS related sources may be expected and still meet the endpoint. Scenario 5 was selected as the final allocation scenario after consultation with DEQ. This scenario was also supported by the modeling team from Olin Corporation and MACTEC, Inc and the Olin Corporation.

Table 5.1 Allocation scenarios for mercury concentration with current loading estimates at outlet of NFHR at state line.

% reduction in:						
	Hg in runoff sediment	Hg in interflow	Hg in groundwater	Hg in Atmospheric deposition	Hg in point Sources and FCPS sources	% of time 90-day median exceeds 2 (ng/L) endpoint
Existing Conditions	0	0	0	0	0	100.0%
Scenario 01	80	0	0	0	0	90.6%
Scenario 02	80	20	0	20	0	66.1%
Scenario 03	80	20	0	20	80	0.0%
Scenario 04	80	20	0	20	75	0.0%
Scenario 05	80	20	0	20	52	0.0%
Scenario 06	50	20	0	20	90	24.5%
Scenario 07	70	20	0	20	90	0.0%
Scenario 08	90	20	0	20	25	0.0%
Scenario 09	72	20	0	20	72	0.0%
Scenario 10	80	20	10	20	42	0.0%

Highlighted scenario is selected as the final allocation scenario

Table 5.2 shows the necessary reductions to meet the mercury endpoint in the North Fork Holston River. The table lists the existing contribution of each source, the necessary reduction percentage, and the remaining load after allocation.

Table 5.2 Mercury loading under existing and allocated conditions.

Source	Existing Load (grams per year)	Percent Reduction	Allocated Load (grams per year)
Hg in runoff sediment	20,666	80%	4,133
Hg in interflow	515	20%	412
Hg in groundwater	170	0%	170
Hg in atmospheric deposition	20	20%	16
Hg in point sources	28	52%	13
Hg in FCPS sources	256	52%	123
Total	21,655	78%	4,867

Figure 5.3 shows the allocated hourly simulated concentration, 90-day existing and allocated medians, and the 2 ng/L endpoint. The allocated concentrations are a result of running model using Scenario 5 at the watershed outlet (Virginia/Tennessee state line).

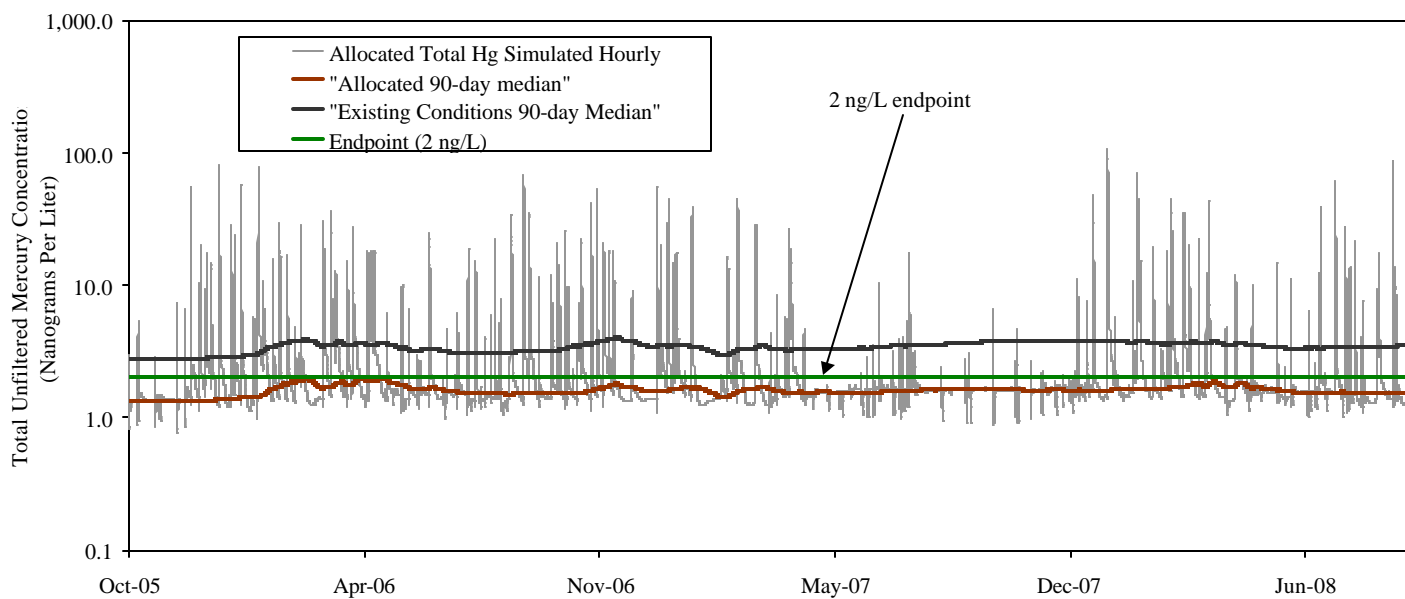


Figure 5.3 Allocated and existing 90-day median, hourly simulated mercury concentration, and 2 ng/L endpoint at the watershed outlet.

Table 5.3, is known as the annual TMDL table, gives the number of grams of mercury that can reach the stream in a given year and still meet the endpoint. These numbers are divided into Waste Load Allocation (WLA) (the portion of mercury that may come from permitted discharge sources) and Load Allocation (LA) (the portion of mercury that may come from the non-permitted non-point sources existing in the watershed). The margin of safety was applied implicitly as described in Section 5.1.

Table 5.3 Total maximum daily load of mercury expressed as an average annual grams.

WLA (grams per year)	LA (grams per year)	MOS	TMDL (grams per year)
13	4,854	<i>Implicit</i>	4,867

Current USEPA guidelines requires that the NFHR TMDL be expressed as daily load. To accomplish this, the annual TMDL was divided by 365 to obtain the average daily load in grams as shown in Table 5.4. Since daily flow fluctuates around the median and is not steady on a daily basis, and since the load is influenced by storm events, a maximum daily load was calculated and is shown in Table 5.5. The maximum daily load was estimated as the 95th percentile of the daily loads during simulation period. The WLA was estimated the same way the average daily WLA since no regular measurements of mercury were taken from point sources to assess variability. In both daily tables (Table 5.4 and Table 5.5), the load allocation (LA) was estimated by subtracting the WLA from the TMDL. The load in Table 5.5 may be tolerated on a non-regular basis and will result in non-compliance with the endpoint if it were exceeded more often than five percent of the time.

Table 5.4 Total maximum daily load of mercury expressed as an average daily grams.

WLA (grams per day)	LA (grams per day)	MOS	TMDL (grams per day)
0.022	13.294	<i>Implicit</i>	13.334

Table 5.5 Total maximum daily load of mercury expressed as a maximum daily grams.

WLA (grams per day)	LA (grams per day)	MOS	TMDL (grams per day)
0.022	52.491	<i>Implicit</i>	52.531

6. TMDL IMPLEMENTATION AND REASONABLE ASSURANCE

Once a TMDL has been approved by EPA, measures must be taken to reduce pollution levels from both point and nonpoint sources. The following sections outline the framework used in Virginia to provide reasonable assurance that the required pollutant reductions can be achieved. The TMDL discussed here deals with a situation where many measures have already been taken to reduce mercury influx to the stream.

6.1 Continuing Planning Process and Water Quality Management Planning

As part of the Continuing Planning Process, VADEQ staff will present both EPA-approved TMDLs and TMDL implementation plans to the State Water Control Board (SWCB) for inclusion in the appropriate Water Quality Management Plan (WQMP), in accordance with the Clean Water Act's Section 303(e) and Virginia's Public Participation Guidelines for Water Quality Management Planning.

VADEQ staff will also request that the SWCB adopt TMDL WLAs as part of the Water Quality Management Planning Regulation (9VAC 25-720), except in those cases when permit limitations are equivalent to numeric criteria contained in the Virginia Water Quality Standards, such as in the case for bacteria. This regulatory action is in accordance with §2.2-4006A.4.c and §2.2-4006B of the Code of Virginia. SWCB actions relating to water quality management planning are described in the public participation guidelines referenced above and can be found on the VADEQ web site under www.deq.state.va.us/export/sites/default/tmdl/pdf/ppp.pdf.

6.2 Staged Implementation

In general, Virginia intends for the recommended control actions, including Best Management Practices (BMPs), to be implemented in an iterative process that first addresses those sources with the largest impact on water quality. The iterative implementation of pollution control actions in the watershed has several benefits:

1. It enables tracking of water quality improvements following implementation through follow-up stream monitoring;

2. It provides a measure of quality control, given the uncertainties inherent in computer simulation modeling;
3. It provides a mechanism for developing public support through periodic updates on implementation levels and water quality improvements;
4. It helps ensure that the most cost effective practices are implemented first; and
5. It allows for the evaluation of the adequacy of the TMDL in achieving water quality standards.

The amount of management practices needed for attaining the required reductions will be determined during the implementation plan phase of the process.

6.3 Implementation of Waste Load Allocations

Federal regulations require that all new or revised National Pollutant Discharge Elimination System (NPDES) permits must be consistent with the assumptions and requirements of any applicable TMDL WLA (40 CFR §122.44 (d)(1)(vii)(B)). All such permits should be submitted to EPA for review.

For the implementation of the WLA component of the TMDL, the Commonwealth utilizes the Virginia NPDES program. Requirements of the permit process should not be duplicated in the TMDL process, and permitted sources are not usually addressed through the development of any TMDL implementation plans.

6.4 Implementation of Load Allocations

The TMDL program does not impart new implementation authorities. Therefore, the Commonwealth intends to use existing programs to the fullest extent in order to attain its water quality goals. The measures for nonpoint source reductions, which can include the use of better treatment technology and the installation of best management practices (BMPs), are implemented in an iterative process that is described along with specific BMPs in the TMDL implementation plan.

6.4.1 Implementation Plan Development

For the implementation of the TMDL's LA component, a TMDL implementation plan will be developed that addresses at a minimum the requirements specified in the Code of

Virginia, Section 62.1-44.19:7. State law directs the State Water Control Board to “develop and implement a plan to achieve fully supporting status for impaired waters”. The implementation plan “shall include the date of expected achievement of water quality objectives, measurable goals, corrective actions necessary and the associated costs, benefits and environmental impacts of addressing the impairments”. EPA outlines the minimum elements of an approvable implementation plan in its 1999 “Guidance for Water Quality-Based Decisions: The TMDL Process”. The listed elements include implementation actions/management measures, timelines, legal or regulatory controls, time required to attain water quality standards, monitoring plans and milestones for attaining water quality standards.

In order to qualify for other funding sources, such as EPA’s Section 319 grants, additional plan requirements may need to be met. The detailed process for developing an implementation plan has been described in the “TMDL Implementation Plan Guidance Manual”, published in July 2003. It is available upon request from the VADEQ and VADCR TMDL project staff or at www.deq.virginia.gov/tmdl/implans/fpguide.pdf.

Watershed stakeholders will have opportunities to provide input and to participate in the development of the TMDL implementation plan. Regional and local offices of VADEQ, VADCR, and other cooperating agencies are technical resources to assist in this endeavor.

With successful completion of implementation plans, local stakeholders will have a blueprint to restore impaired waters and enhance the value of their land and water resources. Additionally, development of an approved implementation plan may enhance opportunities for obtaining financial and technical assistance during implementation.

6.4.2 Staged Implementation Scenarios

The purpose of the staged implementation scenarios is to identify one or more combinations of implementation actions that result in the reduction of controllable sources to the maximum extent practicable using cost-effective, reasonable BMPs for nonpoint source control. One approach would be to identify and quantify the management practices necessary to achieved the desired reductions and implement half

of those measures in the first stage of implementation. With continued monitoring and assessment of mercury levels in fish tissue, a decision will then be made as to whether the implementation of the remaining management practices is necessary. Any management practice that is aimed at reducing sediment influx to the river is deemed appropriate for reducing mercury loadings as well. The first stage of implementation can focus on management practices that have a higher return for the money spent by implementing the more cost-effective measures first.

Actions identified during TMDL implementation plan development that go beyond what can be considered cost-effective and reasonable will only be included as implementation actions if there are reasonable grounds for assuming that these actions will in fact be effective.

If water quality standards are not met upon implementation of all cost-effective and reasonable BMPs, a Use Attainability Analysis (UAA) may need to be initiated since Virginia's water quality standards allow for changes to use designations if existing water quality standards cannot be attained by implementing effluent limits required under §301b and §306 of Clean Water Act, and by implementing cost effective and reasonable BMPs for nonpoint source control. Additional information on UAAs is presented in Section 6.6.

6.4.3 Link to Ongoing Restoration Efforts

Implementation of this TMDL will contribute to on-going water quality improvement efforts aimed at restoring water quality in the NFHR. Among the on-going efforts are the efforts by Olin Corporation. Most notably of these efforts were dredging river sediment in 1982, completing the construction of an impermeable cap over the 75-acre waste disposal area known as Pond 5 and a permeable cap over the 45-acre waste disposal area known as Pond 6 during Fall 2002. A wildlife habitat area has been created on the former disposal ponds. Olin is operating an on-site water treatment plant for leachate from Ponds 5 and 6. The treatment plant is designed to remove mercury. These efforts continue to show improvement in the water quality indicators related to mercury contamination. A full description of these efforts is available in Appendix A.

Among other on-going efforts are those by USEPA air quality regulations such as the Clean Air Interstate Rule (CAIR) and more specifically, the Clean Air Mercury Rule (CAMR) which are aimed at reducing mercury emissions primarily from coal-fired power plants. In addition, other TMDLs are being developed in the region for other pollutants such as bacteria and sediment. The implementation of such TMDLs will have a direct impact on mercury levels in the NFHR since many management practices that address bacteria and sediment also reduce mercury loading to the river.

6.4.4 Implementation Funding Sources

The implementation of pollutant reductions from non-regulated nonpoint sources relies heavily on incentive-based programs. Therefore, the identification of funding sources for non-regulated implementation activities is a key to success. Cooperating agencies, organizations and stakeholders must identify potential funding sources available for implementation during the development of the implementation plan in accordance with the “Virginia Guidance Manual for Total Maximum Daily Load Implementation Plans”. The TMDL Implementation Plan Guidance Manual contains information on a variety of funding sources, as well as government agencies that might support implementation efforts and suggestions for integrating TMDL implementation with other watershed planning efforts.

Some of the major potential sources of funding for non-regulated implementation actions may include the U.S. Department of Agriculture’s Conservation Reserve Enhancement and Environmental Quality Incentive Programs, EPA Section 319 funds, the Virginia State Revolving Loan Program (also available for permitted activities), Virginia Agricultural Best Management Practices Cost-Share Programs, the Virginia Water Quality Improvement Fund (available for both point and nonpoint source pollution), tax credits and landowner contributions.

With additional appropriations for the Water Quality Improvement Fund during the last two legislative sessions, the Fund has become a significant funding source for agricultural BMPs and wastewater treatment plants. Additionally, funding is being made available to address urban and residential water quality problems. Information on WQIF

projects and allocations can be found at www.deq.virginia.gov/bay/wqif.html and at www.dcr.virginia.gov/soil_&_water/wqia.shtml.

6.5 Follow-Up Monitoring

Following the development of the TMDL, VADEQ will make every effort to continue to monitor the NFHR in accordance with its ambient and biological monitoring programs. VADEQ's Ambient Watershed Monitoring Plan for conventional pollutants calls for watershed monitoring to take place on a rotating basis, bi-monthly for two consecutive years of a six-year cycle. In accordance with *DEQ Guidance Memo No. 03-2004* (www.deq.virginia.gov/waterguidance/pdf/032004.pdf), during periods of reduced resources, monitoring can temporarily discontinue until the TMDL staff determines that implementation measures to address the source(s) of impairments are being installed. Monitoring can resume at the start of the following fiscal year, next scheduled monitoring station rotation, or where deemed necessary by the regional office or TMDL staff, as a new special study.

The purpose, location, parameters, frequency, and duration of the monitoring will be determined by the VADEQ staff, in cooperation with VADCR staff, the Implementation Plan Steering Committee and local stakeholders. Whenever possible, the location of the follow-up monitoring station(s) will be the same as the listing station. At a minimum, the monitoring station must be representative of the original impaired segment. The details of the follow-up monitoring will be outlined in the Annual Water Monitoring Plan prepared by each VADEQ Regional Office. Other agency personnel, watershed stakeholders, etc. may provide input on the Annual Water Monitoring Plan. These recommendations must be made to the VADEQ regional TMDL coordinator by September 30 of each year.

VADEQ staff, in cooperation with VADCR staff, the Implementation Plan Steering Committee and local stakeholders, will continue to use data from the ambient monitoring stations to evaluate reductions in pollutants ("water quality milestones" as established in the IP), the effectiveness of the TMDL in attaining and maintaining water quality standards, and the success of implementation efforts. Recommendations may then be

made, when necessary, to target implementation efforts in specific areas and continue or discontinue monitoring at follow-up stations.

In some cases, watersheds will require monitoring above and beyond what is included in VADEQ's standard monitoring plan. Ancillary monitoring by citizens' or watershed groups, local government, or universities is an option that may be used in such cases. An effort should be made to ensure that ancillary monitoring follows established QA/QC guidelines in order to maximize compatibility with VADEQ monitoring data. In instances where citizens' monitoring data are not available and additional monitoring is needed to assess the effectiveness of targeting efforts, TMDL staff may request of the monitoring managers in each regional office an increase in the number of stations or to monitor existing stations at a higher frequency in the watershed. The additional monitoring beyond the original bimonthly single station monitoring will be contingent on staff resources and available laboratory budget. More information on citizen monitoring in Virginia and QA/QC guidelines is available at www.deq.virginia.gov/cmonitor/.

To demonstrate that the watershed is meeting water quality standards in watersheds where corrective actions have taken place (whether or not a TMDL or Implementation plan has been completed), VADEQ must meet the minimum data requirements from the original listing station or a station representative of the originally listed segment. The minimum data requirement for conventional pollutants (bacteria, dissolved oxygen, etc) is bimonthly monitoring for two consecutive years. For biological monitoring, the minimum requirement is two consecutive samples (one in the spring and one in the fall) in a one year period.

In addition to DEQ monitoring, Olin Corporation will likely continue to monitor fish tissue and sediment concentrations at several locations along the river to fulfill requirements under USEPA Superfund.

6.6 Attainability of Designated Uses

In some streams for which TMDLs have been developed, factors may prevent the stream from attaining its designated use.

In order for a stream to be assigned a new designated use, or a subcategory of a use, the current designated use must be removed. To remove a designated use, the state must demonstrate that the use is not an existing use, and that downstream uses are protected. Such uses will be attained by implementing effluent limits required under §301b and §306 of Clean Water Act and by implementing cost-effective and reasonable best management practices for nonpoint source control (9 VAC 25-260-10 paragraph I).

The state must also demonstrate that attaining the designated use is not feasible because:

1. Naturally occurring pollutant concentration prevents the attainment of the use;
2. Natural, ephemeral, intermittent or low flow conditions prevent the attainment of the use unless these conditions may be compensated for by the discharge of sufficient volume of effluent discharges without violating state water conservation;
3. Human-caused conditions or sources of pollution prevent the attainment of the use and cannot be remedied or would cause more environmental damage to correct than to leave in place;
4. Dams, diversions or other types of hydrologic modifications preclude the attainment of the use, and it is not feasible to restore the waterbody to its original condition or to operate the modification in such a way that would result in the attainment of the use;
5. Physical conditions related to natural features of the water body, such as the lack of proper substrate, cover, flow, depth, pools, riffles, and the like, unrelated to water quality, preclude attainment of aquatic life use protection; or
6. Controls more stringent than those required by §301b and §306 of the Clean Water Act would result in substantial and widespread economic and social impact.

This and other information is collected through a special study called a UAA. All site-specific criteria or designated use changes must be adopted by the SWCB as amendments to the water quality standards regulations. During the regulatory process, watershed stakeholders and other interested citizens, as well as the EPA, will be able to provide comment. Additional information can be obtained at www.deq.virginia.gov/wqs/designated.html.

The process to address potentially unattainable reductions based on the above is as follows:

As a first step, measures targeted at the controllable sources identified in the TMDL's staged implementation scenarios will be implemented. The expectation is that all controllable sources would be reduced to the maximum extent possible using the implementation approaches described above. VADEQ will continue to monitor biological health and water quality in the stream during and subsequent to the implementation of these measures to determine if the water quality standard is attained. This effort will also help to evaluate if the modeling assumptions were correct. In the best-case scenario, water quality goals will be met and the stream's uses fully restored using effluent controls and BMPs. If, however, water quality standards are not being met, and no additional effluent controls and BMPs can be identified, a UAA would then be initiated with the goal of re-designating the stream for a more appropriate use or subcategory of a use.

A 2006 amendment to the Code of Virginia under 62.1-44.19:7E. provides an opportunity for aggrieved parties in the TMDL process to present to the State Water Control Board reasonable grounds indicating that the attainment of the designated use for a water is not feasible. The Board may then allow the aggrieved party to conduct a use attainability analysis according to the criteria listed above and a schedule established by the Board. The amendment further states that "If applicable, the schedule shall also address whether TMDL development or implementation for the water shall be delayed".

7. PUBLIC PARTICIPATION

Public participation during TMDL development for the North Fork Holston River was encouraged; a summary of the meetings is presented in Table 7.1. The first public meeting was held at two locations due to the large size of the area addressed by this TMDL. Two meetings were held on November 4, 2008 at Friend's Community Church in Saltville, Virginia. The first meeting was the Technical Advisory Committee (TAC) meeting and the second was the first of two public meetings. During the TAC meeting, preliminary sources assessment and modeling results were discussed. The second of two first public meetings was held at the Hilton Elementary School at Hiltons, Virginia on November 6, 2008. During both public meeting, the impairment issue was introduced to the public along with a description of steps to follow and accomplishments up to that date. The meetings were publicized by placing notices in the Virginia Register, and electronic mail advertisement to all agencies. A press release was also issued and picked up by several local newspapers.

Table 7.1 Public participation during TMDL development for the North Fork Holston River.

Date	Location	Type	Format
11/4/2008	Friend's Community Church in Saltville, Virginia	(First) First Public Meeting	Open to public at large
11/4/2008	Friend's Community Church in Saltville, Virginia	First TAC Meeting	
11/6/2008	Hilton Elementary School, Hiltons, Virginia	(Second) First Public Meeting	Open to public at large
1/25/2010	Friend's Community Church in Saltville, Virginia	(First) Final Public Meeting	Open to public at large
1/25/2010	Friend's Community Church in Saltville, Virginia	Second TAC Meeting	
1/26/2010	Hilton Elementary School, Hiltons, Virginia	(Second) Final Public Meeting	Open to public at large

The final public meeting was held at two locations due to the large size of the area addressed by this TMDL. Two meetings were held on January 25, 2010 at Friend's Community Church in Saltville, Virginia. The first meeting was the Technical Advisory Committee (TAC) meeting and the second was the first of two final public meetings. The second of two final public meetings was held at the Hilton Elementary School at Hiltons, Virginia on January 26, 2010. During the public meetings, the public was informed of the findings of the TMDL project and given the chance to comment on these findings. The public was informed of what steps follow the final public meetings.

Public participation during the implementation plan development process will include the formation of a stakeholders' committee as well as open public meetings. Public participation is critical to promote reasonable assurances that the implementation activities will occur. A stakeholders' committee will have the express purpose of formulating the TMDL Implementation Plan. The major stakeholders were identified during the development of this TMDL. The committee will consist of, but not be limited to, representatives from VADEQ, VADCR, and local governments. This committee will have the responsibility for identifying corrective actions that are founded in practicality, establishing a time line to insure expeditious implementation, and setting measurable goals and milestones for attaining water quality standards.

GLOSSARY

Note: All entries in italics are taken from USEPA (1998).

303(d). A section of the Clean Water Act of 1972 requiring states to identify and list water bodies that do not meet the states' water quality standards.

Allocations. That portion of a receiving water's loading capacity attributed to one of its existing or future pollution sources (nonpoint or point) or to natural background sources. (A wasteload allocation [WLA] is that portion of the loading capacity allocated to an existing or future point source, and a load allocation [LA] is that portion allocated to an existing or future nonpoint source or to natural background levels. Load allocations are best estimates of the loading, which can range from reasonably accurate estimates to gross allotments, depending on the availability of data and appropriate techniques for predicting loading.)

Ambient water quality. Natural concentration of water quality constituents prior to mixing of either point or nonpoint source load of contaminants. Reference ambient concentration is used to indicate the concentration of a chemical that will not cause adverse impact on human health.

Anthropogenic. Pertains to the [environmental] influence of human activities.

Aquatic ecosystem. Complex of biotic and abiotic components of natural waters. The aquatic ecosystem is an ecological unit that includes the physical characteristics (such as flow or velocity and depth), the biological community of the water column and benthos, and the chemical characteristics such as dissolved solids, dissolved oxygen, and nutrients. Both living and nonliving components of the aquatic ecosystem interact and influence the properties and status of each component.

Assimilative capacity. The amount of contaminant load that can be discharged to a specific waterbody without exceeding water quality standards or criteria. Assimilative capacity is used to define the ability of a waterbody to naturally absorb and use a discharged substance without impairing water quality or harming aquatic life.

Background levels. Levels representing the chemical, physical, and biological conditions that would result from natural geomorphological processes such as weathering or dissolution.

Bacteria. Single-celled microorganisms. Bacteria of the coliform group are considered the primary indicators of fecal contamination and are often used to assess water quality.

Bacterial decomposition. Breakdown by oxidation, or decay, of organic matter by heterotrophic bacteria. Bacteria use the organic carbon in organic matter as the energy source for cell synthesis.

Bacterial source tracking (BST). A collection of scientific methods used to track sources of fecal contamination.

Benthic. Refers to material, especially sediment, at the bottom of an aquatic ecosystem. It can be used to describe the organisms that live on, or in, the bottom of a waterbody.

Benthic organisms. Organisms living in, or on, bottom substrates in aquatic ecosystems.

Best management practices (BMPs). *Methods, measures, or practices determined to be reasonable and cost-effective means for a landowner to meet certain, generally nonpoint source, pollution control needs. BMPs include structural and nonstructural controls and operation and maintenance procedures.*

Bioassessment. Evaluation of the condition of an ecosystem that uses biological surveys and other direct measurements of the resident biota. (2)

Biochemical Oxygen Demand (BOD). Represents the amount of oxygen consumed by bacteria as they break down organic matter in the water.

Biometric. (Biological Metric) The study of biological phenomena by measurements and statistics.

Biosolids. Biologically treated solids originating from municipal wastewater treatment plants.

Box and whisker plot. A graphical representation of the mean, lower quartile, upper quartile, upper limit, lower limit, and outliers of a data set.

Calibration. *The process of adjusting model parameters within physically defensible ranges until the resulting predictions give a best possible good fit to observed data.*

Cause. 1. That which produces an effect (a general definition).

2. A stressor or set of stressors that occur at an intensity, duration and frequency of exposure that results in a change in the ecological condition (a SI-specific definition).

Channel. *A natural stream that conveys water; a ditch or channel excavated for the flow of water.*

Clean Water Act (CWA). *The Clean Water Act (formerly referred to as the Federal Water Pollution Control Act or Federal Water Pollution Control Act Amendments of 1972), Public Law 92-500, as amended by Public Law 96-483 and Public Law 97-117, 33 U.S.C. 1251 et seq. The Clean Water Act (CWA) contains a number of provisions to restore and maintain the quality of the nation's water resources. One of these provisions is Section 303(d), which establishes the TMDL program.*

Concentration. *Amount of a substance or material in a given unit volume of solution; usually measured in milligrams per liter (mg/L) or parts per million (ppm).*

Concentration-response model. A quantitative (usually statistical) model of the relationship between the concentration of a chemical to which a population or community of organisms is exposed and the frequency or magnitude of a biological response. (2)

Confluence. The point at which a river and its tributary flow together.

Contamination. *The act of polluting or making impure; any indication of chemical, sediment, or biological impurities.*

Continuous discharge. *A discharge that occurs without interruption throughout the operating hours of a facility, except for infrequent shutdowns for maintenance, process changes, or other similar activities.*

Conventional pollutants. As specified under the Clean Water Act, conventional contaminants include suspended solids, coliform bacteria, high biochemical oxygen demand, pH, and oil and grease.

Critical condition. The critical condition can be thought of as the "worst case" scenario of environmental conditions in the waterbody in which the loading expressed in the TMDL for the pollutant of concern will continue to meet water quality standards. Critical conditions are the combination of environmental factors (e.g., flow, temperature, etc.) that results in attaining and maintaining the water quality criterion and has an acceptably low frequency of occurrence.

Decay. The gradual decrease in the amount of a given substance in a given system due to various sink processes including chemical and biological transformation, dissipation to other environmental media, or deposition into storage areas.

Designated uses. Those uses specified in water quality standards for each waterbody or segment whether or not they are being attained.

Dilution. The addition of some quantity of less-concentrated liquid (water) that results in a decrease in the original concentration.

Direct runoff. Water that flows over the ground surface or through the ground directly into streams, rivers, and lakes.

Discharge. Flow of surface water in a stream or canal, or the outflow of groundwater from a flowing artesian well, ditch, or spring. Can also apply to discharge of liquid effluent from a facility or to chemical emissions into the air through designated venting mechanisms.

Discharge Monitoring Report (DMR). Report of effluent characteristics submitted by a municipal or industrial facility that has been granted an NPDES discharge permit.

Discharge permits (under NPDES). A permit issued by the EPA or a state regulatory agency that sets specific limits on the type and amount of pollutants that a municipality or industry can discharge to a receiving water; it also includes a compliance schedule for achieving those limits. The permit process was established under the National Pollutant Discharge Elimination System, under provisions of the Federal Clean Water Act.

Dissolved Oxygen (DO). The amount of oxygen in water. DO is a measure of the amount of oxygen available for biochemical activity in a waterbody.

Domestic wastewater. Also called sanitary wastewater, consists of wastewater discharged from residences and from commercial, institutional, and similar facilities.

Drainage basin. A part of a land area enclosed by a topographic divide from which direct surface runoff from precipitation normally drains by gravity into a receiving water. Also referred to as a watershed, river basin, or hydrologic unit.

Dynamic model. A mathematical formulation describing and simulating the physical behavior of a system or a process and its temporal variability.

Ecoregion. A region defined in part by its shared characteristics. These include meteorological factors, elevation, plant and animal speciation, landscape position, and soils.

Effluent. *Municipal sewage or industrial liquid waste (untreated, partially treated, or completely treated) that flows out of a treatment plant, septic system, pipe, etc.*

Effluent guidelines. *The national effluent guidelines and standards specify the achievable effluent pollutant reduction that is attainable based upon the performance of treatment technologies employed within an industrial category. The National Effluent Guidelines Program was established with a phased approach whereby industry would first be required to meet interim limitations based on best practicable control technology currently available for existing sources (BPT). The second level of effluent limitations to be attained by industry was referred to as best available technology economically achievable (BAT), which was established primarily for the control of toxic pollutants.*

Effluent limitation. *Restrictions established by a state or EPA on quantities, rates, and concentrations in pollutant discharges.*

Endpoint. *An endpoint (or indicator/target) is a characteristic of an ecosystem that may be affected by exposure to a stressor. Assessment endpoints and measurement endpoints are two distinct types of endpoints commonly used by resource managers. An assessment endpoint is the formal expression of a valued environmental characteristic and should have societal relevance (an indicator). A measurement endpoint is the expression of an observed or measured response to a stress or disturbance. It is a measurable environmental characteristic that is related to the valued environmental characteristic chosen as the assessment endpoint. The numeric criteria that are part of traditional water quality standards are good examples of measurement endpoints (targets).*

Erosion. The detachment and transport of soil particles by water and wind. Sediment resulting from soil erosion represents the single largest source of nonpoint pollution in the United States.

Eutrophication. The process of enrichment of water bodies by nutrients. Waters receiving excessive nutrients may become eutrophic, are often undesirable for recreation, and may not support normal fish populations.

Evapotranspiration. The combined effects of evaporation and transpiration on the water balance. Evaporation is water loss into the atmosphere from soil and water surfaces. Transpiration is water loss into the atmosphere as part of the life cycle of plants.

Fate of pollutants. *Physical, chemical, and biological transformation in the nature and changes of the amount of a pollutant in an environmental system. Transformation processes are pollutant-specific. Because they have comparable kinetics, different formulations for each pollutant are not required.*

Fecal Coliform. Indicator organisms (organisms indicating presence of pathogens) associated with the digestive tract.

General Standard. A narrative standard that ensures the general health of state waters. All state waters, including wetlands, shall be free from substances attributable to sewage,

industrial waste, or other waste in concentrations, amounts, or combinations which contravene established standards or interfere directly or indirectly with designated uses of such water or which are inimical or harmful to human, animal, plant, or aquatic life (9VAC25-260-20). (4)

Geometric mean. A measure of the central tendency of a data set that minimizes the effects of extreme values.

GIS. Geographic Information System. A system of hardware, software, data, people, organizations and institutional arrangements for collecting, storing, analyzing and disseminating information about areas of the earth. (Dueker and Kjerne, 1989)

Ground water. *The supply of fresh water found beneath the earth's surface, usually in aquifers, which supply wells and springs. Because ground water is a major source of drinking water, there is growing concern over contamination from leaching agricultural or industrial pollutants and leaking underground storage tanks.*

HSPF. Hydrological Simulation Program – Fortran. A computer simulation tool used to mathematically model nonpoint source pollution sources and movement of pollutants in a watershed.

Hydrologic cycle. *The circuit of water movement from the atmosphere to the earth and its return to the atmosphere through various stages or processes, such as precipitation, interception, runoff, infiltration, storage, evaporation, and transpiration.*

Hydrology. *The study of the distribution, properties, and effects of water on the earth's surface, in the soil and underlying rocks, and in the atmosphere.*

Impairment. A detrimental effect on the biological integrity of a water body that prevents attainment of the designated use.

IMPLND. An impervious land segment in HSPF. It is used to model land covered by impervious materials, such as pavement.

Indicator organism. *An organism used to indicate the potential presence of other (usually pathogenic) organisms. Indicator organisms are usually associated with the other organisms, but are usually more easily sampled and measured.*

Interflow. Runoff that travels just below the surface of the soil.

Isolate. An inbreeding biological population that is isolated from similar populations by physical or other means.

Leachate. *Water that collects contaminants as it trickles through wastes, pesticides, or fertilizers. Leaching can occur in farming areas, feedlots, and landfills and can result in hazardous substances entering surface water, ground water, or soil.*

Limits (upper and lower). The lower limit equals the lower quartile – 1.5x(upper quartile – lower quartile), and the upper limit equals the upper quartile + 1.5x(upper quartile – lower quartile). Values outside these limits are referred to as outliers.

Loading, Load, Loading rate. *The total amount of material (pollutants) entering the system from one or multiple sources; measured as a rate in weight per unit time.*

Load allocation (LA). *The portion of a receiving waters loading capacity attributed either to one of its existing or future nonpoint sources of pollution or to natural background sources. Load allocations are best estimates of the loading, which can range from reasonably accurate estimates to gross allotments, depending on the availability of data and appropriate techniques for predicting the loading. Wherever possible, natural and nonpoint source loads should be distinguished (40 CFR 130.2(g)).*

Loading capacity (LC). *The greatest amount of loading a water can receive without violating water quality standards.*

Margin of safety (MOS). *A required component of the TMDL that accounts for the uncertainty about the relationship between the pollutant loads and the quality of the receiving waterbody (CWA Section 303(d)(1)(C)). The MOS is normally incorporated into the conservative assumptions used to develop TMDLs (generally within the calculations or models) and approved by the EPA either individually or in state/EPA agreements. If the MOS needs to be larger than that which is allowed through the conservative assumptions, additional MOS can be added as a separate component of the TMDL (in this case, quantitatively, a $TMDL = LC = WLA + LA + MOS$).*

Mass balance. *An equation that accounts for the flux of mass going into a defined area and the flux of mass leaving the defined area. The flux in must equal the flux out.*

Mass loading. *The quantity of a pollutant transported to a waterbody.*

Mean. *The sum of the values in a data set divided by the number of values in the data set.*

Metrics. *Indices or parameters used to measure some aspect or characteristic of a water body's biological integrity. The metric changes in some predictable way with changes in water quality or habitat condition.*

Metric ton (Mg or t). *A unit of mass equivalent to 1,000 kilograms. An annual load of a pollutant is typically reported in metric tons per year (t/yr).*

MGD. *Million gallons per day. A unit of water flow, whether discharge or withdraw.*

Mitigation. *Actions taken to avoid, reduce, or compensate for the effects of environmental damage. Among the broad spectrum of possible actions are those that restore, enhance, create, or replace damaged ecosystems.*

Model. *Mathematical representation of hydrologic and water quality processes. Effects of land use, slope, soil characteristics, and management practices are included.*

Monitoring. *Periodic or continuous surveillance or testing to determine the level of compliance with statutory requirements and/or pollutant levels in various media or in humans, plants, and animals.*

Mood's Median Test. *A nonparametric (distribution-free) test used to test the equality of medians from two or more populations.*

Narrative criteria. *Nonquantitative guidelines that describe the desired water quality goals.*

National Pollutant Discharge Elimination System (NPDES). *The national program for issuing, modifying, revoking and re-issuing, terminating, monitoring, and enforcing permits, and imposing and enforcing pretreatment requirements, under sections 307, 402, 318, and 405 of the Clean Water Act.*

Natural waters. *Flowing water within a physical system that has developed without human intervention, in which natural processes continue to take place.*

Nonpoint source. *Pollution that originates from multiple sources over a relatively large area. Nonpoint sources can be divided into source activities related to either land or water use including failing septic tanks, improper animal-keeping practices, forest practices, and urban and rural runoff.*

Numeric targets. *A measurable value determined for the pollutant of concern, which, if achieved, is expected to result in the attainment of water quality standards in the listed waterbody.*

Numerical model. *Model that approximates a solution of governing partial differential equations, which describe a natural process. The approximation uses a numerical discretization of the space and time components of the system or process.*

Nutrient. *An element or compound essential to life, including carbon, oxygen, nitrogen, phosphorus, and many others: as a pollutant, any element or compound, such as phosphorus or nitrogen, that in excessive amounts contributes to abnormally high growth of algae, reducing light and oxygen in aquatic ecosystems.*

Organic matter. *The organic fraction that includes plant and animal residue at various stages of decomposition, cells and tissues of soil organisms, and substances synthesized by the soil population. Commonly determined as the amount of organic material contained in a soil or water sample.*

Parameter. *A numerical descriptive measure of a population. Since it is based on the observations of the population, its value is almost always unknown.*

Peak runoff. *The highest value of the stage or discharge attained by a flood or storm event; also referred to as flood peak or peak discharge.*

PERLND. *A pervious land segment in HSPF. It is used to model a particular land use segment within a subwatershed (e.g., pasture, urban land, or crop land).*

Permit. *An authorization, license, or equivalent control document issued by the EPA or an approved federal, state, or local agency to implement the requirements of an environmental regulation; e.g., a permit to operate a wastewater treatment plant or to operate a facility that may generate harmful emissions.*

Permit Compliance System (PCS). *Computerized management information system that contains data on NPDES permit-holding facilities. PCS keeps extensive records on more than 65,000 active water-discharge permits on sites located throughout the nation. PCS tracks permit, compliance, and enforcement status of NPDES facilities.*

Phased/staged approach. *Under the phased approach to TMDL development, load allocations and wasteload allocations are calculated using the best available data and*

information recognizing the need for additional monitoring data to accurately characterize sources and loadings. The phased approach is typically employed when nonpoint sources dominate. It provides for the implementation of load reduction strategies while collecting additional data.

Point source. Pollutant loads discharged at a specific location from pipes, outfalls, and conveyance channels from either municipal wastewater treatment plants or industrial waste treatment facilities. Point sources can also include pollutant loads contributed by tributaries to the main receiving water stream or river.

Pollutant. Dredged spoil, solid waste, incinerator residue, sewage, garbage, sewage sludge, munitions, chemical wastes, biological materials, radioactive materials, heat, wrecked or discarded equipment, rock, sand, cellar dirt, and industrial, municipal, and agricultural waste discharged into water. (CWA section 502(6)).

Pollution. Generally, the presence of matter or energy whose nature, location, or quantity produces undesired environmental effects. Under the Clean Water Act, for example, the term is defined as the man-made or man-induced alteration of the physical, biological, chemical, and radiological integrity of water.

Privately owned treatment works. Any device or system that is (a) used to treat wastes from any facility whose operator is not the operator of the treatment works and (b) not a publicly owned treatment works.

Public comment period. The time allowed for the public to express its views and concerns regarding action by the EPA or states (e.g., a Federal Register notice of a proposed rule-making, a public notice of a draft permit, or a Notice of Intent to Deny).

Publicly owned treatment works (POTW). Any device or system used in the treatment (including recycling and reclamation) of municipal sewage or industrial wastes of a liquid nature that is owned by a state or municipality. This definition includes sewers, pipes, or other conveyances only if they convey wastewater to a POTW providing treatment.

Quartile. The 25th, 50th, and 75th percentiles of a data set. A percentile (p) of a data set ordered by magnitude is the value that has at most p% of the measurements in the data set below it, and (100-p)% above it. The 50th quartile is also known as the median. The 25th and 75th quartiles are referred to as the lower and upper quartiles, respectively.

Rapid Bioassessment Protocol II (RBP II). A suite of measurements based on a quantitative assessment of benthic macroinvertebrates and a qualitative assessment of their habitat. RBP II scores are compared to a reference condition or conditions to determine to what degree a water body may be biologically impaired.

Reach. Segment of a stream or river.

Receiving waters. Creeks, streams, rivers, lakes, estuaries, ground-water formations, or other bodies of water into which surface water and/or treated or untreated waste are discharged, either naturally or in man-made systems.

Reference Conditions. The chemical, physical, or biological quality or condition exhibited at either a single site or an aggregation of sites that are representative of non-

impaired conditions for a watershed of a certain size, land use distribution, and other related characteristics. Reference conditions are used to describe reference sites.

Re-mining. Extracting resources from land previously mined. This method is often used to reclaim abandoned mine areas.

Reserve capacity. Pollutant loading rate set aside in determining stream waste load allocation, accounting for uncertainty and future growth.

Residence time. Length of time that a pollutant remains within a section of a stream or river. The residence time is determined by the streamflow and the volume of the river reach or the average stream velocity and the length of the river reach.

Restoration. Return of an ecosystem to a close approximation of its presumed condition prior to disturbance.

Riparian areas. Areas bordering streams, lakes, rivers, and other watercourses. These areas have high water tables and support plants that require saturated soils during all or part of the year. Riparian areas include both wetland and upland zones.

Riparian zone. The border or banks of a stream. Although this term is sometimes used interchangeably with floodplain, the riparian zone is generally regarded as relatively narrow compared to a floodplain. The duration of flooding is generally much shorter, and the timing less predictable, in a riparian zone than in a river floodplain.

Roughness coefficient. A factor in velocity and discharge formulas representing the effects of channel roughness on energy losses in flowing water. Manning's "n" is a commonly used roughness coefficient.

Runoff. That part of precipitation, snowmelt, or irrigation water that runs off the land into streams or other surface water. It can carry pollutants from the air and land into receiving waters.

Seasonal Kendall test. A statistical tool used to test for trends in data, which is unaffected by seasonal cycles. (Gilbert, 1987)

Sediment. In the context of water quality, soil particles, sand, and minerals dislodged from the land and deposited into aquatic systems as a result of erosion.

Septic system. An on-site system designed to treat and dispose of domestic sewage. A typical septic system consists of a tank that receives waste from a residence or business and a drain field or subsurface absorption system consisting of a series of percolation lines for the disposal of the liquid effluent. Solids (sludge) that remain after decomposition by bacteria in the tank must be pumped out periodically.

Sewer. A channel or conduit that carries wastewater and storm water runoff from the source to a treatment plant or receiving stream. Sanitary sewers carry household, industrial, and commercial waste. Storm sewers carry runoff from rain or snow. Combined sewers handle both.

Simulation. The use of mathematical models to approximate the observed behavior of a natural water system in response to a specific known set of input and forcing conditions.

Models that have been validated, or verified, are then used to predict the response of a natural water system to changes in the input or forcing conditions.

Slope. *The degree of inclination to the horizontal. Usually expressed as a ratio, such as 1:25 or 1 on 25, indicating one unit vertical rise in 25 units of horizontal distance, or in a decimal fraction (0.04), degrees (2 degrees 18 minutes), or percent (4 percent).*

Source. An origination point, area, or entity that releases or emits a stressor. A source can alter the normal intensity, frequency, or duration of a natural attribute, whereby the attribute then becomes a stressor.

Spatial segmentation. *A numerical discretization of the spatial component of a system into one or more dimensions; forms the basis for application of numerical simulation models.*

Staged Implementation. A process that allows for the evaluation of the adequacy of the TMDL in achieving the water quality standard. As stream monitoring continues to occur, staged or phased implementation allows for water quality improvements to be recorded as they are being achieved. It also provides a measure of quality control, and it helps to ensure that the most cost-effective practices are implemented first.

Stakeholder. Any person with a vested interest in the TMDL development.

Standard. In reference to water quality (e.g. 200 cfu/100 mL geometric mean limit).

Standard deviation. A measure of the variability of a data set. The positive square root of the variance of a set of measurements.

Standard error. The standard deviation of a distribution of a sample statistic, esp. when the mean is used as the statistic.

Statistical significance. An indication that the differences being observed are not due to random error. The p-value indicates the probability that the differences are due to random error (i.e. a low p-value indicates statistical significance).

Steady-state model. *Mathematical model of fate and transport that uses constant values of input variables to predict constant values of receiving water quality concentrations. Model variables are treated as not changing with respect to time.*

Storm runoff. *Storm water runoff, snowmelt runoff, and surface runoff and drainage; rainfall that does not evaporate or infiltrate the ground because of impervious land surfaces or a soil infiltration rate lower than rainfall intensity, but instead flows onto adjacent land or into waterbodies or is routed into a drain or sewer system.*

Streamflow. *Discharge that occurs in a natural channel. Although the term "discharge" can be applied to the flow of a canal, the word "streamflow" uniquely describes the discharge in a surface stream course. The term "streamflow" is more general than "runoff" since streamflow may be applied to discharge whether or not it is affected by diversion or regulation.*

Stream Reach. A straight portion of a stream.

Stream restoration. Various techniques used to replicate the hydrological, morphological, and ecological features that have been lost in a stream because of urbanization, farming, or other disturbance.

Stressor. Any physical, chemical, or biological entity that can induce an adverse response.

Surface area. The area of the surface of a waterbody; best measured by planimetry or the use of a geographic information system.

Surface runoff. Precipitation, snowmelt, or irrigation water in excess of what can infiltrate the soil surface and be stored in small surface depressions; a major transporter of nonpoint source pollutants.

Surface water. All water naturally open to the atmosphere (rivers, lakes, reservoirs, ponds, streams, impoundments, seas, estuaries, etc.) and all springs, wells, or other collectors directly influenced by surface water.

Suspended Solids. Usually fine sediments and organic matter. Suspended solids limit sunlight penetration into the water, inhibit oxygen uptake by fish, and alter aquatic habitat.

Technology-based standards. Effluent limitations applicable to direct and indirect sources that are developed on a category-by-category basis using statutory factors, not including water quality effects.

Timestep. An increment of time in modeling terms. The smallest unit of time used in a mathematical simulation model (e.g. 15-minutes, 1-hour, 1-day).

Ton (T). A unit of measure of mass equivalent to 2,200 English lbs.

Topography. The physical features of a geographic surface area including relative elevations and the positions of natural and man-made features.

Total Dissolved Solids (TDS). A measure of the concentration of dissolved inorganic chemicals in water.

Total Maximum Daily Load (TMDL). The sum of the individual wasteload allocations (WLAs) for point sources, load allocations (LAs) for nonpoint sources and natural background, plus a margin of safety (MOS). TMDLs can be expressed in terms of mass per time, toxicity, or other appropriate measures that relate to a state's water quality standard.

TMDL Implementation Plan. A document required by Virginia statute detailing the suite of pollution control measures needed to remediate an impaired stream segment. The plans are also required to include a schedule of actions, costs, and monitoring. Once implemented, the plan should result in the previously impaired water meeting water quality standards and achieving a "fully supporting" use support status.

Transport of pollutants (in water). Transport of pollutants in water involves two main processes: (1) advection, resulting from the flow of water, and (2) dispersion, or transport due to turbulence in the water.

TRC. Total Residual Chlorine. A measure of the effectiveness of chlorinating treated wastewater effluent.

Tributary. A lower order-stream compared to a receiving waterbody. "Tributary to" indicates the largest stream into which the reported stream or tributary flows.

Urban Runoff. Surface runoff originating from an urban drainage area including streets, parking lots, and rooftops.

Validation (of a model). Process of determining how well the mathematical model's computer representation describes the actual behavior of the physical processes under investigation. A validated model will have also been tested to ascertain whether it accurately and correctly solves the equations being used to define the system simulation.

VADACS. Virginia Department of Agriculture and Consumer Services.

VADCR. Virginia Department of Conservation and Recreation.

VADEQ. Virginia Department of Environmental Quality.

DMLR. Virginia Department of mine Land Reclamation.

DMME. Virginia Department of Mines, Minerals, and Energy.

VDH. Virginia Department of Health.

Wasteload allocation (WLA). The portion of a receiving waters' loading capacity that is allocated to one of its existing or future point sources of pollution. WLAs constitute a type of water quality-based effluent limitation (40 CFR 130.2(h)).

Wastewater. Usually refers to effluent from a sewage treatment plant. See also Domestic wastewater.

Wastewater treatment. Chemical, biological, and mechanical procedures applied to an industrial or municipal discharge or to any other sources of contaminated water to remove, reduce, or neutralize contaminants.

Water quality. The biological, chemical, and physical conditions of a waterbody. It is a measure of a waterbody's ability to support beneficial uses.

Water quality-based permit. A permit with an effluent limit more stringent than one based on technology performance. Such limits might be necessary to protect the designated use of receiving waters (e.g., recreation, irrigation, industry, or water supply).

Water quality criteria. Levels of water quality expected to render a body of water suitable for its designated use, composed of numeric and narrative criteria. Numeric criteria are scientifically derived ambient concentrations developed by the EPA or states for various pollutants of concern to protect human health and aquatic life. Narrative criteria are statements that describe the desired water quality goal. Criteria are based on specific levels of pollutants that would make the water harmful if used for drinking, swimming, farming, fish production, or industrial processes.

Water quality standard. Law or regulation that consists of the beneficial designated use or uses of a waterbody, the numeric and narrative water quality criteria that are necessary to protect the use or uses of that particular waterbody, and an antidegradation statement.

Watershed. A drainage area or basin in which all land and water areas drain or flow toward a central collector such as a stream, river, or lake at a lower elevation.

WQIA. Water Quality Improvement Act.

GWLF Hydrologic Parameters:

Watershed Related Parameter Descriptions

Unsaturated Soil Moisture Capacity (SMC): The amount of moisture in the root zone, evaluated as a function of the area-weighted soil type attribute – available water capacity.

Recession Coefficient (/day): The recession coefficient is a measure of the rate at which streamflow recedes following the cessation of a storm, and is approximated by averaging the ratios of streamflow on any given day to that on the following day during a wide range of weather conditions, all during the recession limb of each storm's hydrograph.

Seepage Coefficient (/day): The seepage coefficient represents the amount of flow lost to deep seepage.

Initial unsaturated storage (cm): Initial depth of water stored in the unsaturated (surface) zone.

Initial saturated storage (cm): Initial depth of water stored in the saturated zone.

Initial snow (cm): Initial amount of snow on the ground at the beginning of the simulation.

Antecedent Rainfall for each of 5 previous days (cm): The amount of rainfall on each of the five days preceding the first day in the weather files.

Month Related Parameter Descriptions

Month: Months were ordered, starting with April and ending with March – in keeping with the design of the GWLF model and its assumption that stored sediment is flushed from the system at the end of each Apr-Mar cycle. Model output was modified in order to summarize loads on a calendar year basis.

ET CV: Composite evap-transpiration cover coefficient, calculated as an area-weighted average from land uses within each watershed.

Hours per Day: mean number of daylight hours.

Erosion Coefficient: This a regional coefficient used in Richard's equation for calculating daily erosivity. Each region is assigned separate coefficients for the months October-March, and for April-September.

Sediment Parameters***Watershed-Related Parameter Descriptions***

Sediment Delivery ratio: The fraction of erosion – detached sediment – that is transported or delivered to the edge of the stream, calculated as the inverse function of watershed size (Evans et al., 2001).

Land use-Related Parameter Descriptions

USLE K-factor (erodibility): The soil erodibility factor was calculated as an area weighted average of all component soil types.

USLE LS-factor: This factor is calculated from slope and slope length.

USLE C-factor: The vegetative cover factor for each land use was evaluated following GWLF manual guidance and Wischmeier and Smith (1978).

Daily sediment build-up rate on impervious surfaces: The daily amount of dry deposition deposited from the air on impervious surfaces on days without rainfall, assigned using GWLF manual guidance.

Streambank Erosion Parameter Descriptions (Evans, 2002)

% Developed Land: Percentage of the watershed with urban-related land uses-defined as all land in MDR, HDR, and COM land uses, as well as the impervious portions of LDR.

Animal density: Calculated as the number of beef and dairy 1000-lb equivalent animal units (AU) divided by watershed area in acres.

Stream length: Calculated as the total stream length of natural stream channel, in meters. Excludes the non-erosive hardened and piped sections of the stream.

Stream length with livestock access: calculated as the total stream length in the watershed where livestock have unrestricted access to streams, resulting in streambank trampling, in meters.

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APPENDIX A: HISTORICAL OVERVIEW AND REMEDIATION HISTORY (PROVIDED BY OLIN)

Historical Overview And Remediation History

The Saltville Site was a manufacturing facility for 78 years from 1894 to 1972. Operations included a soda ash plant (1894 to 1970) and a mercury cell chlorine plant (1950 to 1972). All plant operations ceased by 1972 and demolition of the Former Chlorine Plant Site (FCPS) was completed in June 1973.

Regulatory Status

An investigation of the FCPS and NFHR by Olin Corporation, the Commonwealth of Virginia, and local agencies during the late 1960's identified mercury as the constituent of concern. Additional regulatory investigations and actions that followed the initial investigation are presented in Table 1. Virginia and Tennessee implemented a NFHR fishing ban in 1970.

The Site was added to the National Priorities List (NPL) in 1982. Olin signed a Consent Decree in 1988 to implement Interim Remedial Measures and a Remedial Investigation/Feasibility Study (RI/FS). The site was divided into three Operable Units (OU-1 Interim Remedial Measures, OU-2 Source Area Investigations, and OU-3 North Fork Holston River (NFHR) Investigations).

The RI Report (Golder Associates Inc. [Golder], 1994) and Human Health Risk Assessment (HHRA) Report (ABB, 1994) for OU-2 were finalized in 1994. The ecological risk assessment (ERA) was moved from OU-2 to OU-3. The final OU-2 FS Report was submitted in 1995 (Fluor-Daniel, 1995) and USEPA issued the OU-2 Record of Decision (ROD) in September 1995. Olin entered into a Consent Decree in 1997 to implement the remedial actions identified in the ROD for Ponds 5 and 6. Additional studies for the FCPS were combined with the OU-3 NFHR study and were designated as OU-4.

In 2001, Olin received USEPA comments on the Draft OU-3 NFHR RI report (Woodward-Clyde Consultants, 1993) and prepared a work plan for completing the RI. Olin completed additional characterization studies. A Focused RI report for the FCPS was submitted to USEPA in 2004 and subsequently approved by USEPA (Golder, 2004).

A Supplemental RI for OU-4 (NFHR) was submitted in 2006 including an updated ERA and HHRA. Following several additional data collections and evaluations, the Supplemental RI and HHRA were approved by EPA on July 6, 2009 and June 2, 2009, respectively. A FS for OU-4 was submitted on March 18, 2009 and is pending approval.

History of Remedial Actions

Olin began investigating the nature and extent of mercury in soils and groundwater at the Site in 1976. Remediation activities have occurred at the Site over the past 3 decades; beginning in 1978, with installation of erosion control measures, continuing through 2002, with the closure of Ponds 5 and 6, and current operations, maintenance, and monitoring activities. Mercury concentrations in soils, sediments, surface water, and fish have decreased over time as a result of these remedial activities and are discussed further below.

FCPS Soil Cap and Riverbank Stabilization (1978 – 1979) – In order to stabilize the FCPS riverbank, Olin installed erosion control measures and a riverbank armoring system in 1978 and 1979. The erosion control measures included removing and relocating soils with elevated mercury content to the FCPS, regrading the riverbank, and constructing a soil cap over the FCPS with clean top soil combined with a seed mix to reduce erosion. Additional riverbank remediation included placing a layer of clean sand over the regraded area, installing a geotextile filter, and armoring the slope with riprap. Concurrently, a 50 foot section of old FCPS drain lines were removed from behind the remediated riverbank and the remaining lines were plugged with concrete (USEPA, 1981). As a result of capping, soils identified as contaminated with mercury within this area are completely inaccessible.

River Dredging, Disposal Cell, and Cap (1983) – In 1983, Olin removed sediment from approximately 1,000 feet of the NFHR to continue the remediation efforts. A berm was constructed from sediments larger than ½-inch in size adjacent to an old concrete foundation wall to form the disposal cell. A cushioning layer of fine-grained material was placed over the berm sediments and old concrete foundation slabs. A synthetic impermeable fabric was placed over the bottom fine-grained layer to provide additional

protection, followed by construction of a synthetic impermeable lined cell to contain river sediments less than ½-inch in diameter. The fine sediments were encapsulated by sealing the top and bottom liners, and placing a cushioning layer of fine-grained material over the liner. River sediments greater than ½-inch in diameter were used to establish the subgrade elevation. The clay cap was constructed on the subgrade material, and consisted of a layer of up to 2.5 feet of clay, a 1-foot drainage layer, and a vegetative soil cover.

The synthetic liner at the FCPS was installed on a stable base (cushion sand over concrete slab) and backfilled with a stable soil material. As such, movements due to shifting or settlement have not occurred. The liner is buried and has a relatively constant temperature and no ultraviolet exposure and the life expectancy can be considered to be in the range of 200+ years.

To reduce the potential for groundwater seepage discharging to river sediments, approximately 1,000 feet of bedrock exposed during dredging in the river channel was sealed with “shotcrete.” For over 25 years, Olin has maintained the FCPS cap, erosion control measures, and site security measures in accordance with the Consent Special Order. Since 1982, significant statistical decreases in NFHR sediment concentrations have been observed.

Western Diversion Ditch (1982 – 1983) – Olin constructed an open channel diversion ditch to convey surface water run-off from Little Mountain around the northern and western end of Pond 5, eventually discharging these waters to the NFHR. Construction was completed in 1983.

Eastern Diversion Ditch (1991) – Due to the effectiveness of the western diversion ditch, Olin constructed a similar diversion ditch to convey surface water and stormwater run-off from Little Mountain around the eastern part of Pond 5 in 1991. The water is diverted into a high density polyethylene pipe buried under the eastern part of Pond 5. A drop inlet to the pipe collects surface water run-off from drainage areas north-northwest of Pond 5 and the collection system discharges the diverted surface water and stormwater

into the NFHR. The Pond 5 surface water diversion was designated by USEPA as OU-1 upon completion of construction (USEPA, 2007).

Sediment mercury concentrations decreased in the NFHR at RM 77 by approximately half between 1983 and 1991. Benthic macroinvertebrate concentrations decreased by 50 percent adjacent to the Site from 1980 to 1988. Concentrations in algae collected adjacent to the Site from 1980 to 1988 decreased by an order of magnitude. Remediation efforts are believed to be the cause of these concentration reductions in sampled media over time.

Pond 5 Treatment Plant (1992 – 1994) – Olin completed the design and construction of the Pond 5 Treatment Plant in 1992 and 1994, respectively. The Pond 5 outfall was sealed in July 1994 and the treatment plant became operational in November 1994. Since going on line, the Pond 5 Treatment Plant has treated over 290 million gallons of effluent, reducing mercury concentrations in NFHR surface water well below Virginia ambient water quality criterion (0.05 µg/L) and federal ambient water quality (0.12 µg/L) standards at a concentration of 0.0037 µg/L immediately downstream of the FCPS. The Pond 5 Treatment Plant was designated by USEPA as OU-2 upon completion of construction (USEPA, 2007).

Fish tissue mercury concentrations have decreased since the Pond 5 Treatment Plant went online in 1994. The average NFHR filet mercury concentrations showed an approximate decrease of 25 percent in northern hogsucker tissue, approximately 15 percent in rock bass tissue, and approximately 25 percent in sunfish tissue between 1982 and 1994. Between 1994 and 2007, sediment trap samples (e.g., samples of sediments being transported downstream) show a 33 percent decrease immediately downstream of the Site and a 63 percent decrease further downstream at RM 77. Sediment mercury concentrations at RM 77 decreased an additional three fold between 1993 and 2001.

Town Dump Capping (1998) – Olin assisted the Town of Saltville with the installation of a multi-layer cap on the Town Dump in 1998. Olin performed this remediation work for the Town as part of the Virginia Voluntary Remediation Program.

Closure of Ponds 5 and 6 (2001 – 2002) – Between April 2001 and August 2002, Olin constructed a 65-acre “light weight” multi-layer impermeable cap over Pond 5 and a 45-acre permeable soil cover over Pond 6. The closure included the capture and conveyance of the Pond 6 outfall water to the Pond 5 Treatment Plant for pH adjustment. The closure of Ponds 5 and 6 was designated by USEPA as OU-3 upon completion of construction (USEPA, 2007).

Remedial Action Summary – Reductions in mercury and methylmercury concentrations in Asiatic clams, megaloptera, and crayfish have decreased between 58 percent and 76 percent between 1990 and 2002. Smallmouth bass filet average mercury concentrations decreased approximately 35 percent between 2003 and 2007. An Index of Biotic Integrity (IBI) study performed [by MACTEC] in 2005 showed expected species composition and diversity for benthic macroinvertebrates. Compared to historical IBI data, 2005 showed marked improvements in abundance and diversity of fish and macroinvertebrates. NFHR surface water samples collected in 2008 adjacent to Ponds 5 and 6 were below surface water quality criteria. Groundwater concentrations from Ponds 5 and 6 continue to decrease since Ponds 5 and 6 were capped. Fish tissue and sediment concentrations continue to decrease over time at a rate of approximately 2 to 4 percent per year.

APPENDIX B: MODELING PROCEDURE: LINKING THE SOURCES TO THE ENDPOINT

Modeling Procedure: Linking the Sources to the Endpoint

Establishing the relationship between in-stream water quality and the source loadings is a critical component of TMDL development. It allows for the evaluation of management options that will achieve the desired water quality endpoint. In the development of the mercury TMDL in the North Fork Holston River, the relationship was defined through computer modeling based on data collected throughout the watersheds. Monitored flow and water quality data were then used to verify that the relationships developed through modeling were accurate. There are five basic steps in the development and use of a water quality model: model selection, source assessment, selection of a representative modeling period, model calibration, model validation, and model simulation.

Model selection involves identifying an approved model that is capable of simulating the pollutants of interest with the available data. Source assessment involves identifying and quantifying the potential sources of pollutants in the watershed. Selection of a representative period involves the identification of a time period that accounts for critical conditions associated with all potential sources within the watershed. Calibration is the process of comparing modeled data to observed data and making appropriate adjustments to model parameters to minimize the error between observed and simulated events. Validation is the process of comparing modeled data to observed data during a period other than that used for calibration, with the intent of assessing the capability of the model in hydrologic conditions other than those used during calibration. During validation, no adjustments are made to model parameters. Once a suitable model is constructed, the model is then used to predict the effects of current loadings and potential management practices on water quality.

Modeling Framework Selection

The USGS Hydrologic Simulation Program - Fortran (HSPF) water quality model was selected as the modeling framework to simulate existing conditions and to perform TMDL allocations. The HSPF model is a continuous simulation model that can account for NPS pollutants in runoff, as well as pollutants entering the flow channel from point sources. In establishing the existing and allocation conditions, seasonal variations in

hydrology, climatic conditions, and watershed activities were explicitly accounted for in the model. The use of HSPF allowed consideration of seasonal aspects of precipitation patterns within the watershed.

The HSPF model simulates a watershed by dividing it up into a network of stream segments (referred to in the model as RCHRES), impervious land areas (IMPLND) and pervious land areas (PERLND). Each subwatershed contains a single RCHRES, modeled as an open channel, and numerous PERLNDs and IMPLNDs, representing the various land uses in that subwatershed. Water and pollutants from the land segments in a given subwatershed flow into the RCHRES in that subwatershed. Point discharges and withdrawals of water and pollutants are simulated as flowing directly to or withdrawing from a particular RCHRES as well. Water and pollutants from a given RCHRES flow into the next downstream RCHRES. The network of RCHRESs is constructed to mirror the configuration of the stream segments found in the physical world. Therefore, activities simulated in one impaired stream segment affect the water quality downstream in the model.

Model Setup

To adequately represent the spatial variation in the watershed, the North Fork Holston River watershed drainage area was divided into 23 subwatersheds (Figure B.1). The rationale for choosing these subwatersheds was based on the availability of water quality data and the limitations of the HSPF model. Water quality data (*i.e.*, mercury loads and/or concentrations) are available at specific locations throughout the watershed. The spatial division of the watersheds allowed for a more refined representation of pollutant sources, and a more realistic description of hydrologic factors in the watersheds.

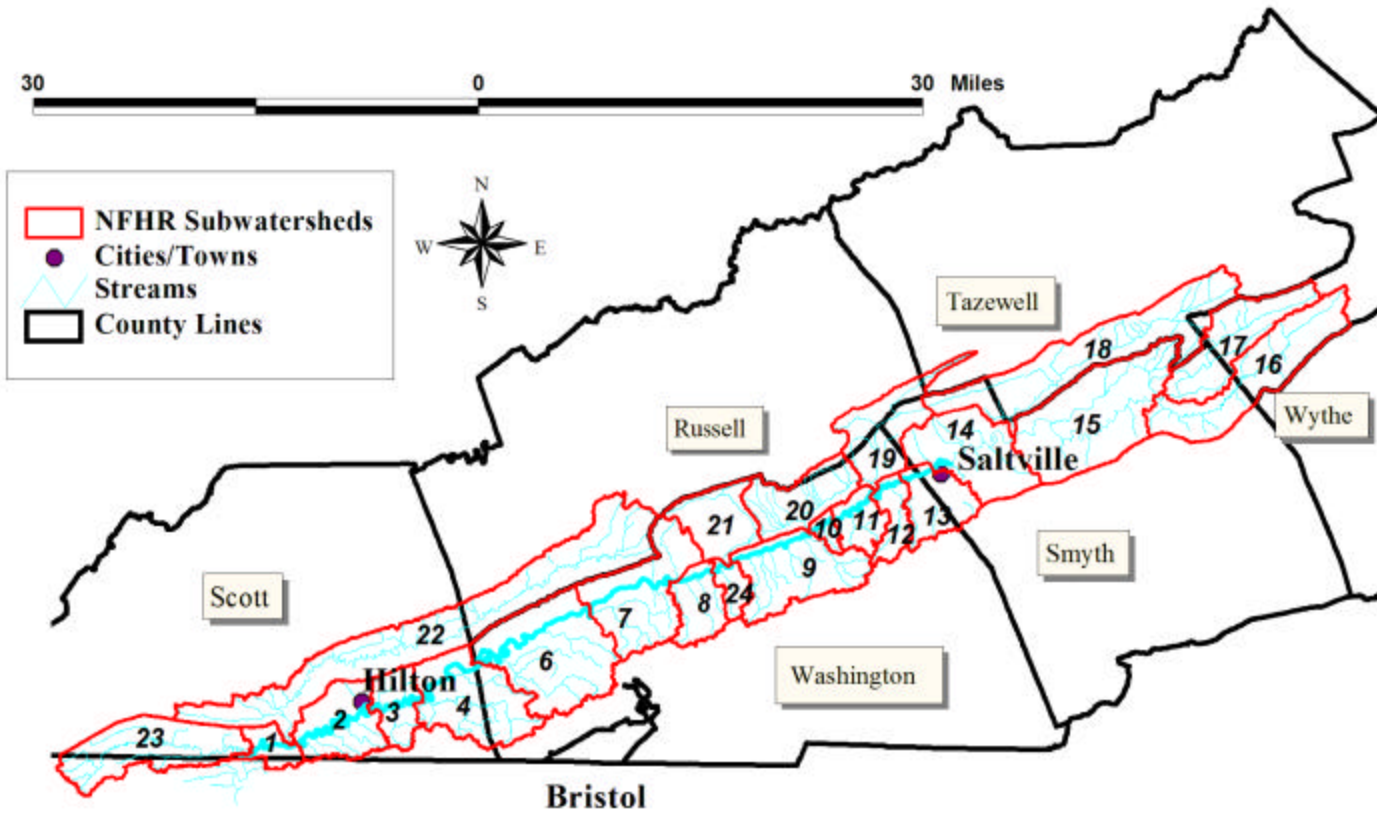


Figure B. 1 Modeling subwatersheds.

Using aerial photographs, MRLC identified 14 land use types in the watersheds. The 14 land use types were consolidated into seven categories based on similarities in hydrologic and waste application/production features (Table B.1). Within each subwatershed, up to the seven land use types were represented. Each land use had parameters associated with it that described the hydrology of the area (*e.g.*, average slope length) and the behavior of pollutants (*e.g.*, mercury concentration in top soil). These land use types are represented in HSPF as pervious land segments (PERLNDs) and impervious land segments (IMPLNDs). Impervious areas in the watershed are represented in three IMPLND types, while there are six PERLND types, each with parameters describing a particular land use (Table B.1). Some IMPLND and PERLND parameters (*e.g.*, slope length) vary with the particular subwatershed in which they are located. Others vary with season such as plant growth.

Table B.1 Consolidation of MRLC land use categories for the North Fork Holston River.

TMDL Land use Categories	Pervious/Impervious (Percentage)	MRLC Land use Classifications (Class No.)
Water	Impervious (100%)	Open Water (11)
Developed	Pervious (75%) Impervious (25%)	Developed, Open Space (21) Developed, Low Intensity (22) Developed, Medium Intensity (23) Developed High Intensity (24)
Barren	Pervious (90%) Impervious (10%)	Barren Land (31)
Woodland	Pervious (100%)	Deciduous Forest (41) Evergreen Forest (42) Mixed Forest (43) Shrub, Scrub (52) Grassland, Herbaceous (71)
Pasture	Pervious (100%)	Pasture, Hay (81)
Cropland	Pervious (100%)	Row Crops (82)
Wetlands	Pervious (100%)	Woody Wetlands (90)

Stream Characteristics

HSPF requires that each stream reach be represented by constant characteristics (*e.g.*, stream geometry and resistance to flow). This data are entered into HSPF via the Hydraulic Function Tables (F-tables). The F-tables developed consist of four columns: depth (ft), area (ac), volume (ac-ft), and outflow (ft³/s). The depth represents the possible range of flow, with a maximum value beyond what would be expected for the reach. The area listed is the surface area of the flow in acres. The volume corresponds to the total volume of the flow in the reach, and is reported in acre-feet. The outflow is simply the stream discharge, in cubic feet per second.

In order to develop the entries for the F-tables, a combination of the NRCS Regional Hydraulic Geometry Curves (NRCS, 2006) and Digital Elevation Models (DEM) was used. The NRCS has developed an empirical formula for estimating stream top width, cross-sectional area, average depth, and flow rate, all as functions of the drainage area. Estimates were obtained at the outlet of each subwatershed. Using the NRCS equations, an entry was developed in the F-table that represented a bank-full situation for the streams. However, the F-table is supposed to cover the floodplains. The floodplain information was obtained from the DEM. A profile perpendicular to the channel was generated showing the floodplain height with distance for each subwatershed outlet. An example of this profile is given in Figure B.2. Consecutive entries to the F-table are generated by estimating the volume of water and surface area in the reach at incremental depths (where depths are taken from the outlet profile, *e.g.* Figure B.2).

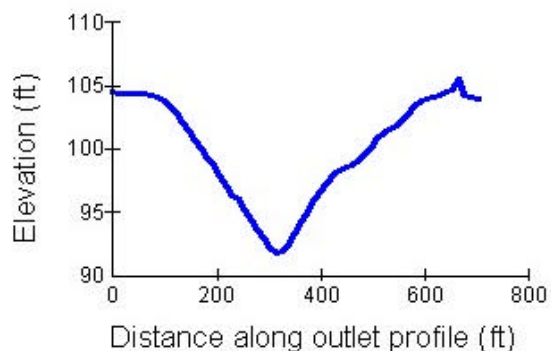


Figure B. 2 Stream profile representation in HSPF.

Selection of Representative Modeling Period

Selection of the modeling period was based on two factors: availability of data (discharge and water-quality) and the need to represent critical hydrological conditions. Mean daily discharge at USGS Gaging Station 03488000 in the North Fork Holston River near Gate City was used. A previous study by DEQ explored the relationship between mean annual flow rate and fish tissue concentration. The study found a good association between preceding year flows and the next year concentrations of mercury in fish tissue since 1997. These results were based on river wide samples. A stronger flow association was found between Rock Bass (0.82) and Sunfish (0.73) with than to N. Hogsuckers (0.45). The study concluded that more data were needed to study the association between flow and fish tissue concentration by river mile.

In order to select a modeling period representative of the critical hydrological condition from the available data, the mean daily flow and precipitation for each season were calculated for the period since 1923. The results of this analysis are shown in Figures B.3 and B.4. This resulted in 85 observations of flow and precipitation for each season. The mean and variance of these observations were calculated. The representative period was chosen such that the mean and variance of each season in the modeled period was not significantly different from the historical data (Table B.2). Therefore, the period was selected as representing the hydrologic regime of the study area, accounting for critical conditions associated with all

potential sources within the watershed. The resulting period for hydrologic calibration was October 1993 to September 1996. For hydrologic validation, the period selected was October 2004 to September 2007.

For water quality calibration, data availability was the governing factor in the choice of calibration and validation periods. The period containing the greatest amount of monitored data dispersed over the most stations. The period for sediment calibration was October 1, 1997 to September 30, 2000 and for sediment validation, October 1, 1994 to September 30, 1997. The period for mercury calibration was April 1, 2008 to September 30, 2008.

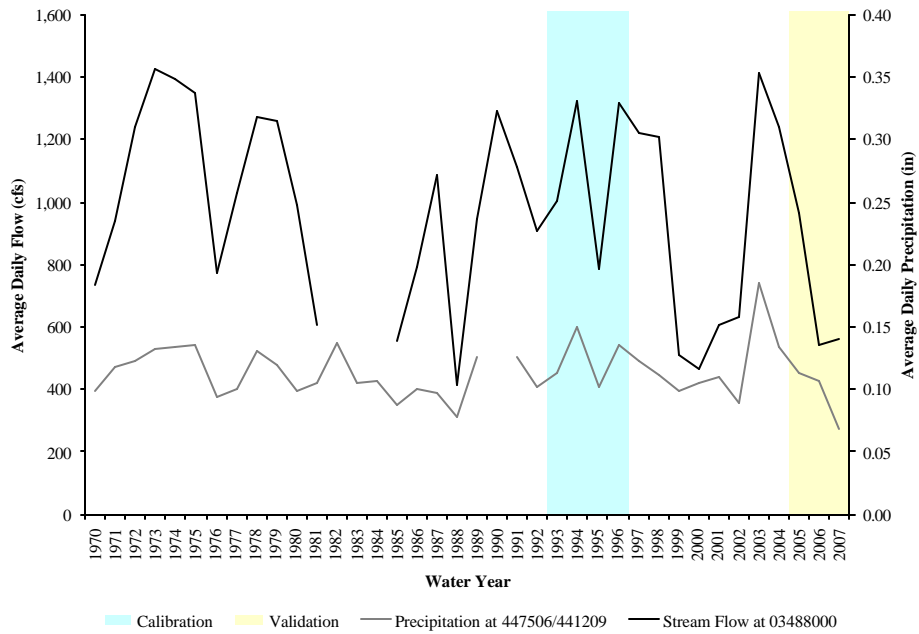


Figure B.3 Annual Historical Flow (USGS Station 03488000) and Precipitation (Stations 442142 and 446906).

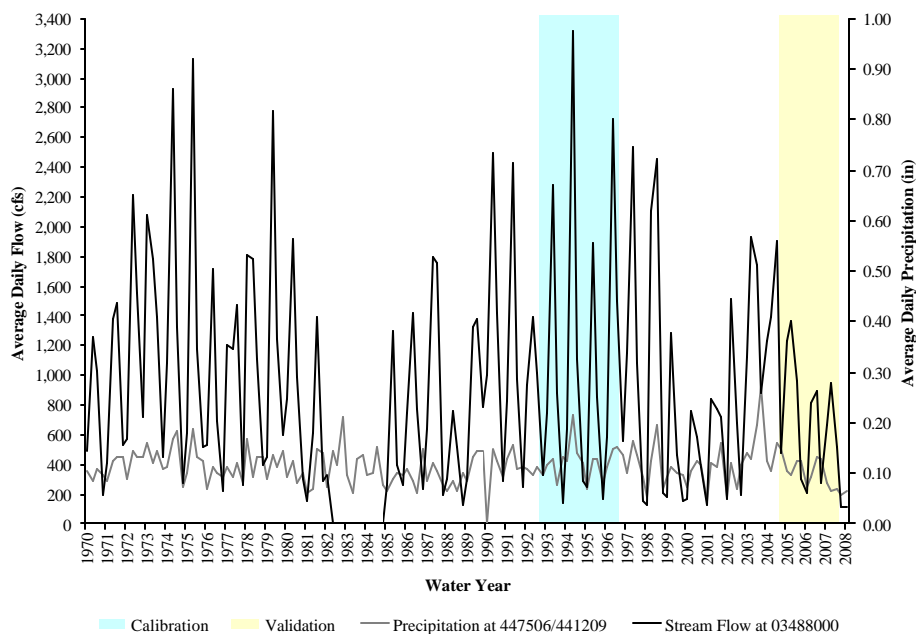


Figure B. 4 Seasonal Historical Flow (USGS Station 03488000) and Precipitation (Stations 442142 and 446906) Data

Table B. 2 Comparison of modeled period to historical records for North Fork Holston River.

	Mean Daily Flow (cfs)				Precipitation (in/day)			
	USGS Station 0348800				Primary Station 442142			
	Fall	Winter	Spring	Summer	Fall	Winter	Spring	Summer
Historical Record (1923-2005)								
Mean	570	1,720	1,006	338	0.0950	0.1234	0.1195	0.1185
Variance	174,404	454,831	164,816	42,759	0.0008	0.0010	0.0009	0.0015
Calibration & Validation Period (10/93 – 09/96, 10/04 – 09/07)								
Mean	617	1,902	959	264	0.0974	0.1253	0.1188	0.1109
Variance	116,781	865,998	88,074	22,412	0.0005	0.0023	0.0010	0.0009
p-Values								
Mean	0.367	0.307	0.351	0.116	0.404	0.458	0.481	0.269
Variance	0.326	0.092	0.220	0.212	0.301	0.046	0.355	0.277

*Secondary Station utilized only when Primary Station was off-line.

Sensitivity Analysis

Sensitivity analyses are performed to determine a model's response to changes in certain parameters. This process involves changing a single parameter a certain percentage from a baseline value while holding all other parameters constant. This process is repeated for several parameters in order to gain a complete picture of the model's behavior. The information gained during sensitivity analysis can aid in model calibration, and it can also help to determine the potential effects of uncertainty in parameter estimation.

Hydrology Sensitivity Analysis

The HSPF parameters adjusted for the hydrologic sensitivity analysis are presented in Table B.3, with base values for the model runs given. The parameters were adjusted to -50%, -10%, 10%, and 50% of the base value, and the model was run for water years 1996-2000. Where an increase of 50% exceeded the maximum value for the parameters, the maximum value was used and the parameters increased over the base value were reported. Peak flows, being a function of runoff, are important because they are directly related to the transport of sediment and mercury from the land surface to the stream. Peak flows were most sensitive to changes in the parameters governing infiltration such as INFILT (Infiltration), LZSN (Lower Zone Storage), and by UZSN (Upper Zone Storage), which governs surface transport, and LZETP (Lower Zone Evapotranspiration), which affects soil moisture. Low flows are important in a water quality model because they control the level of dilution during dry periods. Parameters with the greatest influence on low flows (as evidenced by their influence in the *Low Flows* and *Summer Flow Volume* statistics) were AGWRC (Groundwater Recession Rate), BASETP (Base Flow Evapotranspiration), INFILT, UZSN, LZETP, and CEPSC (Interception Storage Capacity). The responses of these and other hydrologic outputs are reported in Table B.4.

Table B. 3 HSPF base parameter values used to determine hydrologic model response.

Parameter	Description	Units	Base Value
LZSN	Lower Zone Nominal Storage	in	6
INFILT	Soil Infiltration Capacity	in/hr	0.024-0.061
BASETP	Base Flow Evapotranspiration	---	0.01
INTFW	Interflow Inflow	---	2.0
DEEPFR	Groundwater Inflow to Deep Recharge	---	0.11
AGWRC	Groundwater Recession rate	---	0.994
KVARY	Groundwater Recession Flow	1/in	2.0
MON-INTERCEP	Monthly Interception Storage Capacity	in	0.01-0.36
MON-UZSN	Monthly Upper Zone Nominal Storage	in	0.19-1.32
MON-LZETP	Monthly Lower Zone Evapotranspiration	in	0.01-0.4

Table B. 4 HSPF hydrological parameters sensitivity analysis results for NFHR.

Model Parameter	Parameter Change (%)	Total Flow	High Flows	Low Flows	Winter Flow Volume	Spring Flow Volume	Summer Flow Volume	Fall Flow Volume
AGWRC ¹	0.85	2.78	3.83	-13.95	2.49	-0.15	3.31	5.88
AGWRC ¹	0.92	1.26	1.12	-4.05	1.00	0.88	1.18	2.60
AGWRC ¹	0.96	-2.56	-1.81	3.64	-2.01	-2.87	-1.99	-4.89
AGWRC ¹	0.999	-27.86	-16.42	-23.66	-20.08	-37.94	-26.45	-37.61
BASETP	-50	-0.42	-0.61	0.68	-0.32	-0.35	-0.61	-0.26
BASETP	-10	-0.08	-0.12	0.14	-0.06	-0.07	-0.12	-0.05
BASETP	10	0.08	0.12	-0.14	0.06	0.07	0.12	0.05
BASETP	50	0.42	0.61	-0.65	0.32	0.37	0.61	0.26
DEEPFR	-50	2.32	1.01	4.86	1.58	3.42	2.13	3.43
DEEPFR	-10	0.46	0.20	0.97	0.32	0.68	0.42	0.68
DEEPFR	10	-0.46	-0.20	-0.98	-0.31	-0.68	-0.42	-0.68
DEEPFR	50	-2.29	-1.00	-4.89	-1.57	-3.38	-2.09	-3.41
INFILT	-50	7.47	21.94	-16.77	11.42	2.24	10.00	-3.34
INFILT	-10	1.21	3.44	-2.43	1.93	0.14	1.60	-0.43
INFILT	10	-1.13	-3.16	2.13	-1.82	0.01	-1.52	0.34
INFILT	50	-5.09	-13.72	8.70	-8.19	0.76	-7.02	1.08
INTFW	-50	0.43	8.64	-0.70	4.19	-1.61	-0.19	-5.55
INTFW	-10	0.07	1.44	-0.03	0.70	-0.36	0.02	-0.96
INTFW	10	-0.07	-1.33	-0.01	-0.65	0.37	-0.05	0.88
INTFW	50	-0.35	-5.85	-0.11	-2.80	2.18	-0.60	3.78
LZSN	-50	5.25	8.13	-1.71	5.90	4.17	5.89	3.19
LZSN	-10	1.27	1.75	0.02	1.26	1.08	1.47	0.96
LZSN	10	-1.33	-1.77	-0.17	-1.30	-1.14	-1.55	-1.08
LZSN	50	-7.27	-9.09	-2.37	-6.93	-6.17	-8.49	-6.35
CEPSC	-50	-1.72	-4.95	13.62	-1.93	1.17	-4.00	1.19
CEPSC	-10	-0.36	-0.95	2.72	-0.42	0.07	-0.74	0.23
CEPSC	10	0.30	0.84	-2.65	0.31	-0.16	0.69	-0.22
CEPSC	50	1.53	3.87	-10.70	1.42	0.36	3.35	-1.48
LZETP	-50	11.13	14.08	2.13	9.38	10.31	14.11	9.13
LZETP	-10	2.35	2.75	1.06	2.01	2.22	2.83	2.20
LZETP	10	-2.44	-2.74	-1.43	-2.07	-2.31	-2.88	-2.41
LZETP	50	-8.77	-9.37	-6.42	-7.21	-8.40	-10.44	-9.11
KVARY	-50	-1.75	-1.69	6.74	-0.87	-2.79	-2.69	-0.39
KVARY	-10	-0.34	-0.31	1.08	-0.17	-0.53	-0.49	-0.12
KVARY	10	0.34	0.30	-0.96	0.18	0.53	0.48	0.14
KVARY	50	1.68	1.40	-3.85	0.93	2.63	2.29	0.92
UZSN	-50	8.96	14.52	1.08	9.84	3.72	11.52	6.41
UZSN	-10	1.65	2.44	0.43	1.89	0.88	1.85	1.41
UZSN	10	-1.54	-2.26	-0.44	-1.79	-0.82	-1.69	-1.36
UZSN	50	-7.79	-10.90	-3.01	-9.05	-4.28	-8.44	-7.06

¹Actual parameter value used

Water Quality Parameter Sensitivity Analysis

For the water quality sensitivity analysis, an initial base run was performed using precipitation data from the period of mercury calibration on 2008, and model parameters established for 2008 conditions. The impact of changes in precipitation, sediment parameters, and mercury model parameters on resulting mercury concentration in the river was investigated (Table B.5). Parameters with highest impact included precipitation, background mercury levels in top soil, and point sources (including the FCPS related sources).

Table B. 5 Base parameter values used to determine water quality model response.

Description	Original Values	Median of Total Hg (ng/L)		
		-50%	Existing Conditions	+50%
Precipitation	In/yr	0.98	5.56	7.47
KSER (sediment transport)	0.01 - 5	5.31	5.56	5.6
W (settling velocity for silt and clay)	0.0003 – 0.0012 in/sec	6.41	5.56	5.09
TAUCD (critical bed shear stress for deposition)	0.6 lb/ft ²	5.79	5.56	5.37
TAUCS (critical bed shear stress for scour)	0.2 – 0.4 lb/ft ²	6.44	5.56	5.43
M	0.04 – 0.06 lb/ft ² .d	5.52	5.56	5.61
Concentration of mercury in top soil inside of contaminated floodplain	0.12 – 2.3 mg/kg	5.42	5.56	5.70
Concentration of mercury in top soil outside of contaminated floodplain	0.11 mg/kg	4.15	5.56	7.05
Point sources including FCPS related sources	Time series	5.01	5.56	6.24
Atmospheric deposition	13.6 – 30.4 ng/L	5.51	5.56	5.62
Phase transfer rate coefficient (ADRATE)	0.00001 – 20 /day	5.86	5.56	4.77
Adsorption coefficient (KD)	0.1 – 1.0 l/mg	6.52	5.56	5.12

Model Calibration and Validation Processes

Calibration and validation are performed in order to ensure that the model accurately represents the hydrologic and water quality processes in the watershed. The model's hydrologic parameters were set based on available soils, land use, hydrographic, and topographic data. Through calibration, these parameters were adjusted within appropriate ranges until the model performance was deemed acceptable.

Hydrologic Calibration/Validation

HSPF parameters that were adjusted during the hydrologic calibration represented: the amount of evapotranspiration from the root zone (LZETP), the recession rates for groundwater (AGWRC) and interflow (IRC), the amount of soil moisture storage in the upper zone (UZSN) and lower zone (LZSN), the amount of interception storage (CEPSC), the infiltration capacity (INFILT), the amount of soil water contributing to interflow (INTFW), deep groundwater inflow fraction (DEEPER), baseflow PET (BASETP), forest coverage (FOREST), groundwater recession flow (KVARY), maximum and minimum air temperature affecting PET (PETMAX, PETMIN, respectively), infiltration equation exponent (INFEXP), infiltration capacity ratio (INFILD), and active groundwater storage PET (AGWETP). Table B.6 contains the possible range for the above parameters along with the initial estimate and final calibrated value. State variables in the PERLND water (PWAT) section of the User's Control Input (UCI) file were adjusted to reflect initial conditions.

The model was calibrated for hydrologic accuracy using daily flow data from USGS Gaging Station 03488000 on the North Fork Holston River for the period October 1993 through September 1996 (Table B.7). Figures B.5 and B.6 display comparisons of modeled versus observed data for the entire calibration period.

NCDC weather stations Saltville (442142) and Burkes Garden (446906) were used to supply precipitation input for the HSPF model. For the entire modeling period, only daily precipitation values were available, thus daily rainfall values were interpolated to hourly values in order to provide model input on an hourly basis. This interpolation was performed in an HSPF utility called WDMUtil, and is referred to as disaggregation. In

this process, a daily rainfall total is divided up into hourly values using a representative distribution scheme. Daily values were disaggregated using two different schemes: 1) a station matching disaggregation scheme and 2) a triangular disaggregation scheme. The station matching procedure involved identifying a rain gage reporting hourly data in close proximity to the North Fork Holston River whose daily total precipitation was within 5% of the total daily precipitation value of a station within the study area. In this case, the distribution of rainfall at the station within the watershed was disaggregated based on the precipitation pattern reported at the hourly station. When this condition failed, the precipitation was disaggregated based on a triangular distribution, over an 8-hour period.

Table B. 6 Model parameters utilized for hydrologic calibration.

Parameter	Units	Possible Range of Parameter Value	Initial Parameter Estimate	Calibrated Parameter Value
LZSN	in	2.0 – 15.0	3.4-9.6	6
INFILT	in/hr	0.001 – 0.50	0.08-0.2	0.02-0.15
KVARY	l/in	0.0 – 5.0	1	2
AGWRC	l/day	0.85 – 0.999	0.98	0.994
DEEPR	---	0.0 – 0.50	0.1	0.11
BASETP	---	0.0 – 0.20	0.03	0.01
CEPSC	in	0.01 - 0.40	0.01 – 0.2	0.01 – 0.36
UZSN	in	0.05 – 2.0	0.16–1.93	0.19– 1.93
INTFW	---	1.0 – 10.0	1	1
IRC	l/day	0.30 – 0.85	0.50	0.5
LZETP	---	0.1 – 0.9	0.01 – 0.8	0.01 – 0.8

Table B. 7 Hydrology calibration criteria and model performance for period 10/1/1993 through 9/30/1996 at Station 0348800.

Criterion	Observed	Modeled	Error
Total In-stream Flow:	673.17	615.62	-8.55%
Upper 10% Flow Values:	310.98	307.34	-1.17%
Lower 50% Flow Values:	71.60	73.14	2.15%
Winter Flow Volume	380.81	334.31	-12.21%
Spring Flow Volume	169.40	137.39	-18.89%
Summer Flow Volume	50.30	52.54	4.45%
Fall Flow Volume	72.66	91.38	25.76%
Total Storm Volume	623.23	548.60	-11.97%
Winter Storm Volume	368.43	317.69	-13.77%
Spring Storm Volume	156.92	120.64	-23.12%
Summer Storm Volume	37.83	35.82	-5.32%
Fall Storm Volume	60.06	74.46	23.97%

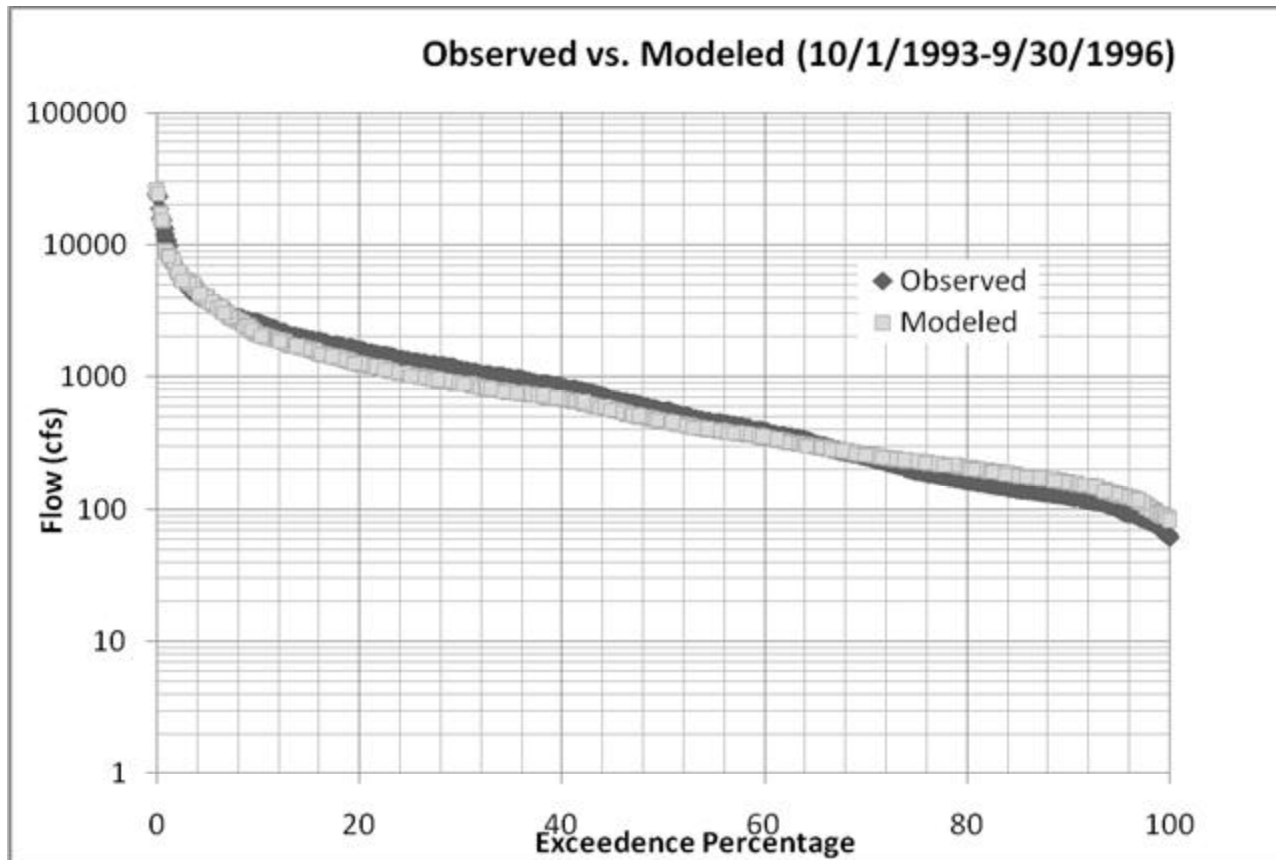


Figure B. 5 North Fork Holston River flow duration at USGS Gaging Station 03488000 for calibration period 10/1/1993 through 9/30/1996.

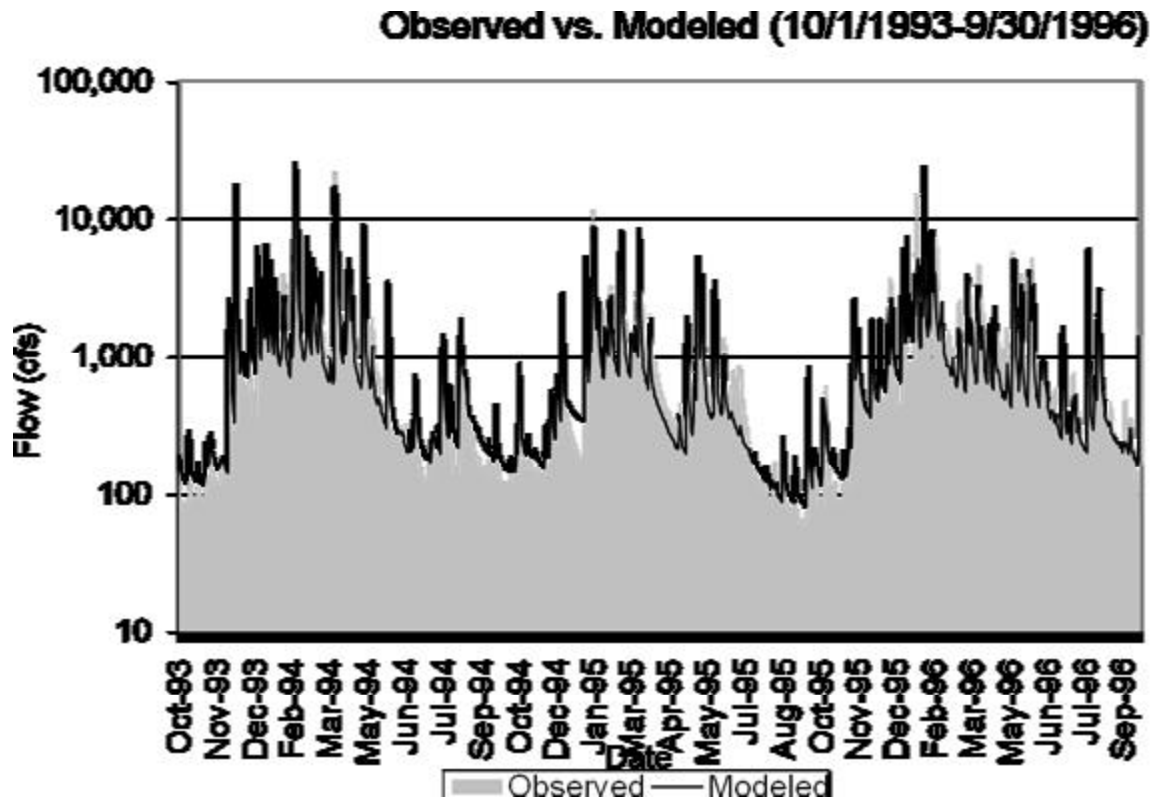


Figure B. 6 Observed and simulated flow Hydrographs for calibration period 10/1/1993 through 9/30/1996 at USGS Gaging Station 03488000.

The hydrologic model was validated using stream flow data from 10/1/2004 to 9/30/2007. The resulting statistics are shown in Table B.8. The percent error is within acceptable ranges for model validation. The hydrology validation results are shown in Figures B.7 and B.8.

Table B.8 Hydrology validation criteria and model performance for North Fork Holston River for the period 10/01/2004 through 9/30/2007.

Criterion	Observed	Modeled	Error
Total In-stream Flow:	406.27	423.16	4.16%
Upper 10% Flow Values:	158.74	171.04	7.75%
Lower 50% Flow Values:	65.58	71.39	8.87%
Winter Flow Volume	151.25	149.78	-0.97%
Spring Flow Volume	116.56	97.93	-15.98%
Summer Flow Volume	34.32	42.09	22.62%
Fall Flow Volume	104.13	133.37	28.07%
Total Storm Volume	361.98	368.76	1.87%
Winter Storm Volume	140.28	136.35	-2.80%
Spring Storm Volume	105.46	84.35	-20.02%
Summer Storm Volume	23.33	28.44	21.90%
Fall Storm Volume	92.91	119.63	28.76%

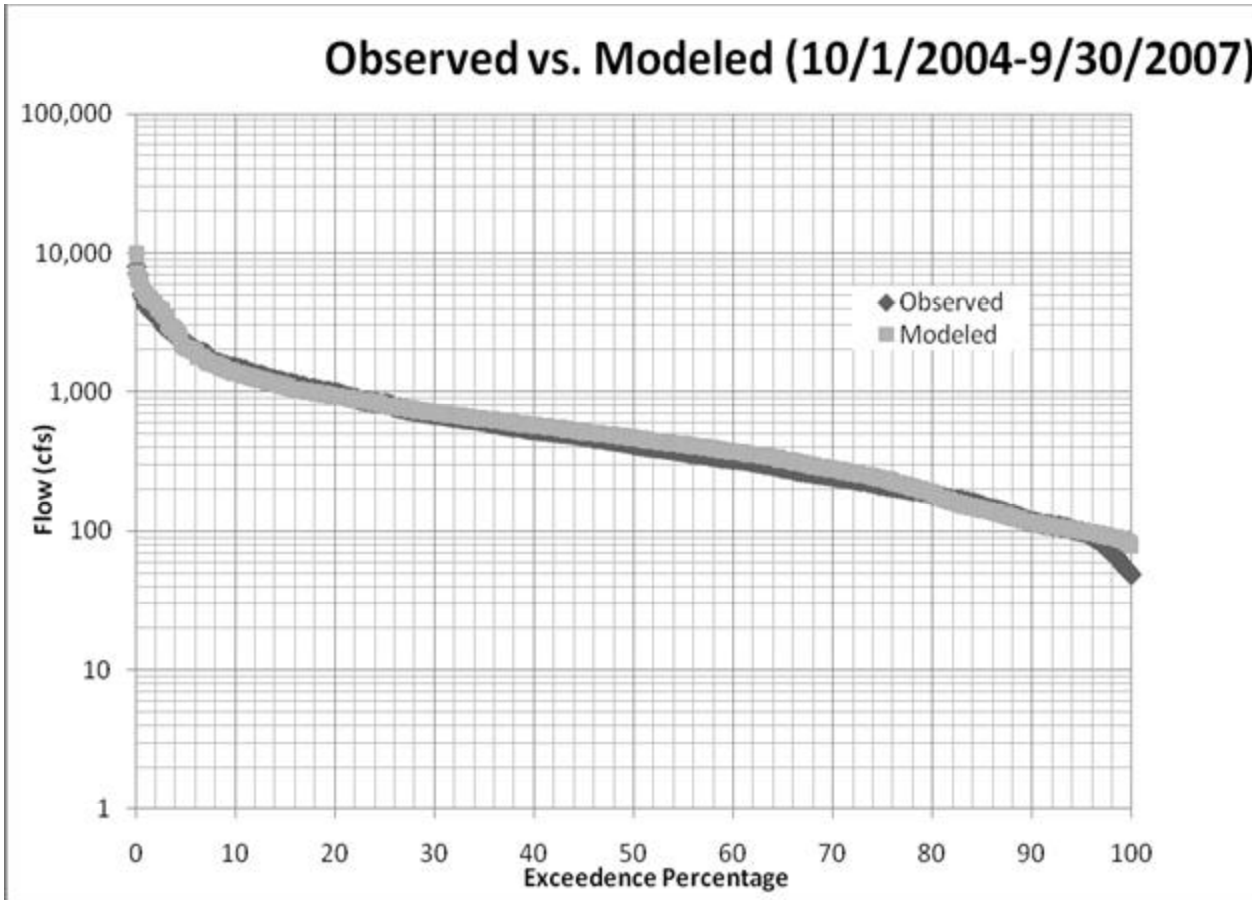


Figure B. 7 North Fork Holston flow duration (10/01/2004 through 09/30/2007).

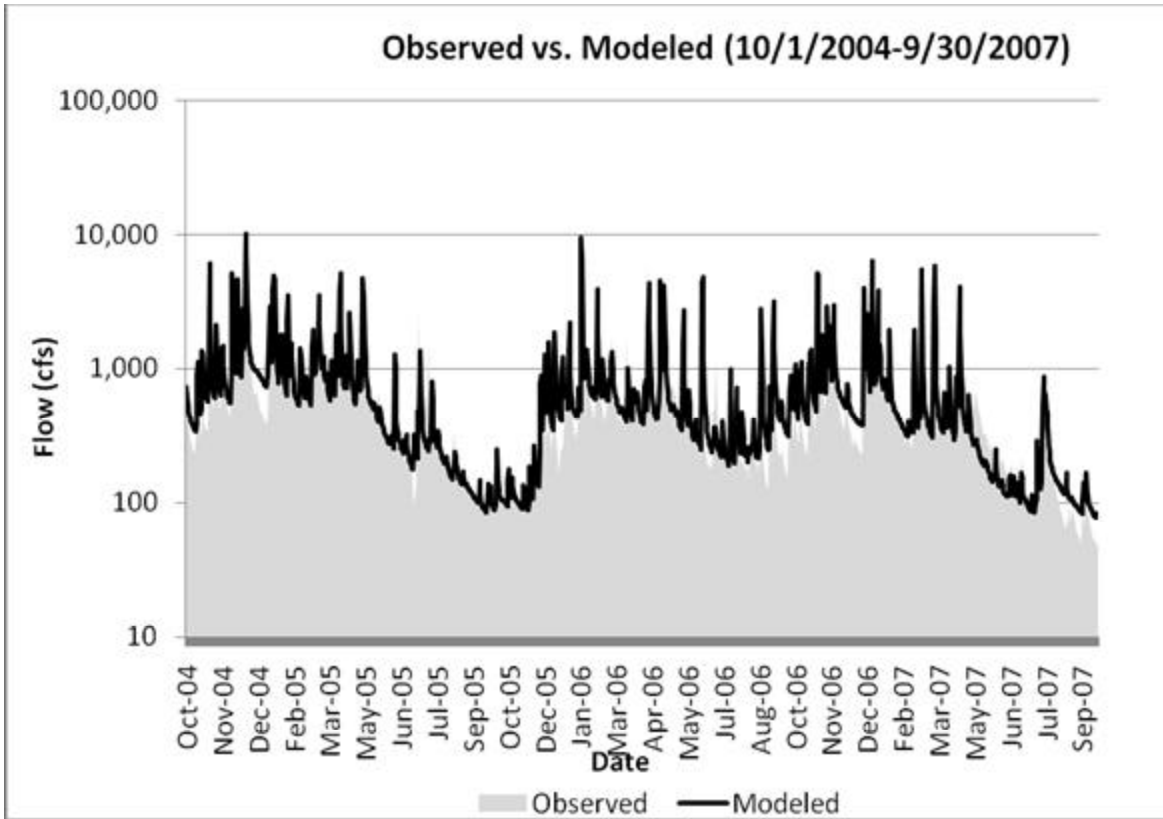


Figure B. 8 Hydrology validation results for North Fork Holston River (10/01/2004 through 09/30/2007).

Sediment Model Calibration/Validation

Before the mercury model was built, a sediment transport model was constructed. Modeling sediment transport properly is vital in modeling mercury transport since sediment is the vehicle on which most mercury transport occurs.

Water quality calibration is complicated by a number of factors, some of which are described here. First, water quality concentrations (e.g. total suspended solids) are highly dependent on flow conditions. Any variability associated with the modeling of stream flow compounds variability in modeling water quality parameters. Second, the concentration of pollutants can be highly variable. Grab samples are collected at a specific point in time and space, while the model predicts concentrations averaged over the entire stream reach and the duration of the time-step.

In HSPF, sediment is modeled as transported from pervious and impervious land segments to streams and rivers during storm events and then further downstream through these streams and rivers. A module named SEDMNT simulates the production and removal of sediment from a pervious land segment (PERLND). An equivalent module for handling solids accumulation and removal from impervious land segments (IMPLND) is called SOLIDS. Finally, the processes of transport, deposition, and scour of sediment within the streams are handled by a module named SEDTRN.

In the SEDMNT module, the user specifies detachment rates. The detached sediment is transported to rivers and streams during runoff events. The user also specifies the rates used in the transport equation. The impervious land segments module allows the user to specify the accumulation and removal rates used by SOLIDS to simulate solids movement. The user also specifies the rates used in the transport equation where solids are transferred during runoff events. Once sediment is in streams, the module SEDTRN simulates the process of deposition on the bed of stream and downstream transportation. Deposited sediment is subject to resuspension. SEDTRN simulates three classes of sediment including clay, silt, and sand. The user specifies transport coefficient rates for each class.

With a successful hydrology calibration, the sediment model was then calibrated. The sediment model calibration was conducted from 10/1/1997 through 9/30/2000. The calibration was conducted at three different locations along the North Fork Holston covering the upper, middle, and lower sections. Data from three DEQ stations at river miles 8.78, 59.65, and 89.25 were used in the analysis. The process involved directly comparing modeled in-stream concentration to observed data and adjusting appropriate model parameters within reasonable ranges. As it was with the hydrologic calibration, the objective of the sediment calibration was to minimize the difference between observed and modeled concentrations.

Several parameters were utilized for model adjustment: coefficient in the sediment washoff equation (KSER), exponent in the sediment washoff equation (JSER), coefficient in the solids washoff equation (KEIM), exponent in the solids washoff equation (JEIM), solids accumulation rate on the land surface (ACCSDP), fraction of solids removed per day (REMSDP), coefficient in sand load power function formula (KSAND), exponent in sand load power function formula (EXPSND), critical bed shear stress for deposition (TAUCD), critical bed shear stress for scour (TAUCS), and erodibility coefficient (M).

All of these parameters were initially set at expected levels for the watershed conditions and adjusted within reasonable limits until an acceptable match between measured and modeled sediment concentrations was established. Table B.9 contains the possible range for the above parameters along with the initial estimate and final calibrated value.

Table B.9 Model parameters utilized for hydrologic calibration.

Parameter	Units	Possible Range of Parameter Value	Initial Parameter Estimate	Calibrated Parameter Value
KSER	complex	0.1 – 10	0.43 – 0.8	0.01 - 5
JSER	none	1 – 3	2	2
KEIM	complex	0.1 – 10	0.03	0.1
JEIM	none	1 – 3	1.8	2
ACCSDP	lb/ac-dy	0.0 – 30	0.01	0.1
REMSDP	per day	0.01 – 1	0.01	0.01
KSAND	complex	0.001 – 10	0.01	0.01
EXPSND	complex	1 – 6	2.0	2.75
TAUCD	lb/ft ²	0.001 – 1	0.3	0.3 – 0.6
TAUCS	lb/ft ²	0.01 – 3	0.3	0.15 – 0.4
M	Lb/ft ² .d	0.001 – 5	0.001	0.2

Results of the calibration are presented in Figures B.9 through B.11. Careful visual inspection of graphical comparisons between continuous simulation results and limited observed points was the primary tool used to guide the calibration process. In addition to visual comparison, basic statistics describing the median, minimum, and maximum of both observed and simulated concentrations were conducted at all three locations (Table B.10). To provide a quantitative measure of the agreement between modeled and measured data while taking the inherent variability of sediment concentrations into account, each observed value was compared with modeled concentrations in a 2day window surrounding the observed data point. Standard error in each observation window was calculated as follows:

$$\text{Standard Error} = \frac{\sqrt{\frac{\sum_{i=1}^n (\text{observed} - \text{modeled}_i)^2}{(n-1)}}}{\sqrt{n}}$$

where

observed = an observed value of sediment concentration

modeled_i = a modeled value in the 2 - day window surrounding the observation

n = the number of modeled observations in the 2 - day window

This is a non-traditional use of standard error, applied here to offer a quantitative measure of model accuracy. In this context, standard error measures the variability of the sample mean of the modeled values about an instantaneous observed value. The use of limited instantaneous observed values to evaluate continuous data introduces error and, therefore, increases standard error. The mean of all standard errors for each station analyzed was calculated. The standard errors shown in Table B.10 are considered an indicator of strong model performance.

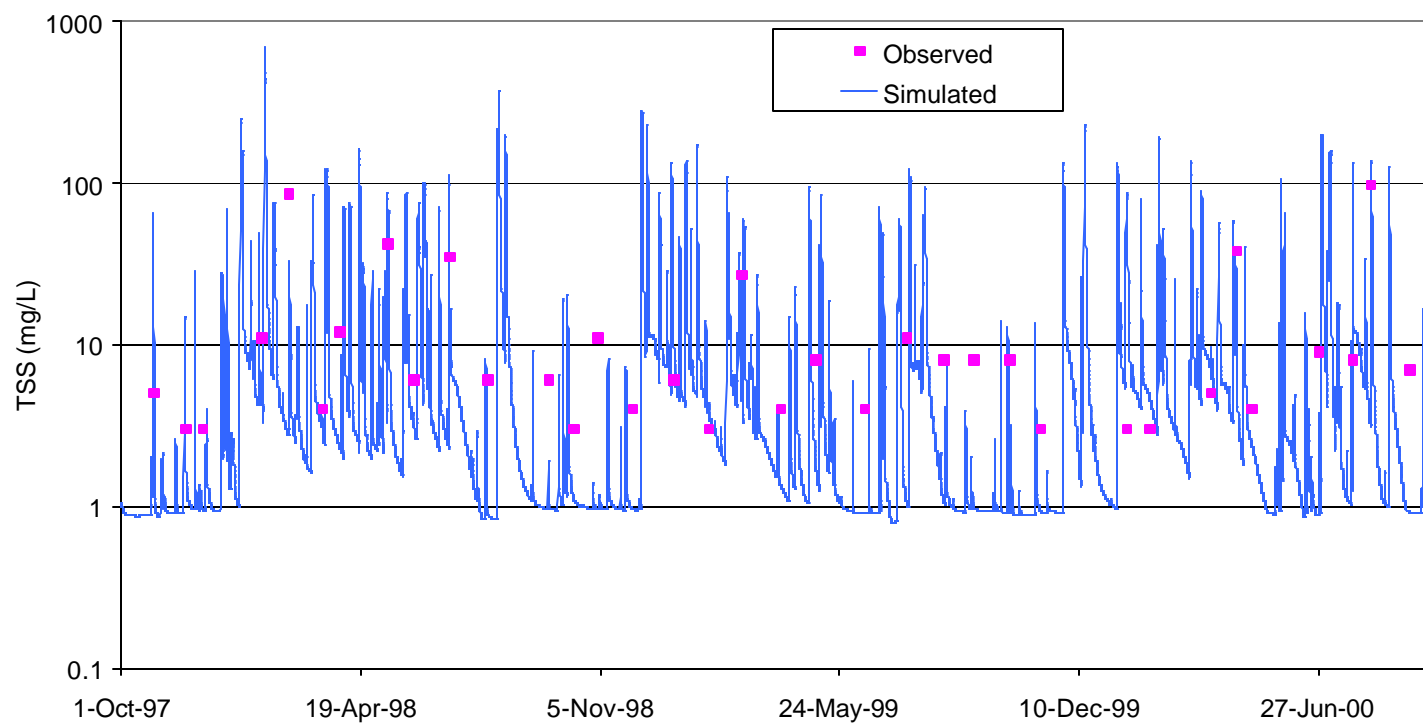


Figure B. 9 Observed and simulated sediment concentration (TSS/100 mL) at DEQ station 6CNFH008.78.

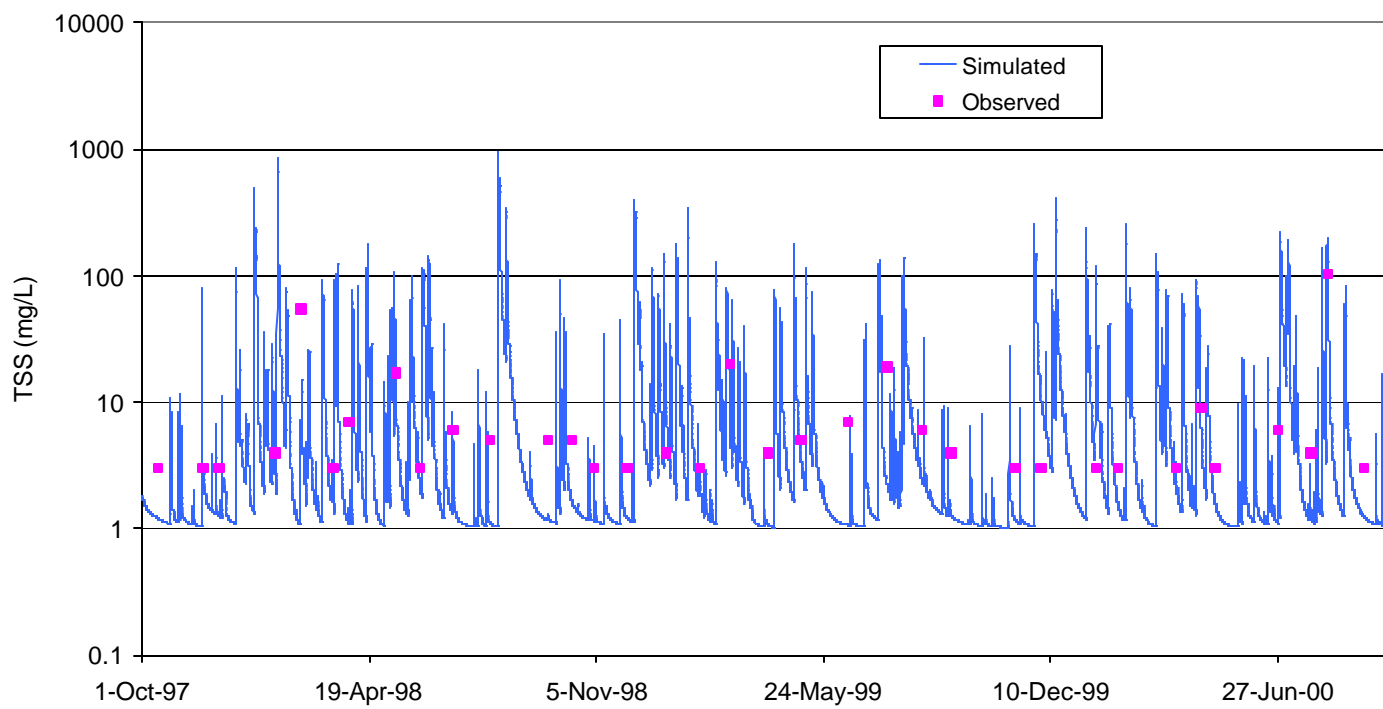


Figure B. 10 Observed and simulated sediment concentration (TSS/100 mL) at DEQ station 6CNFH059.65.

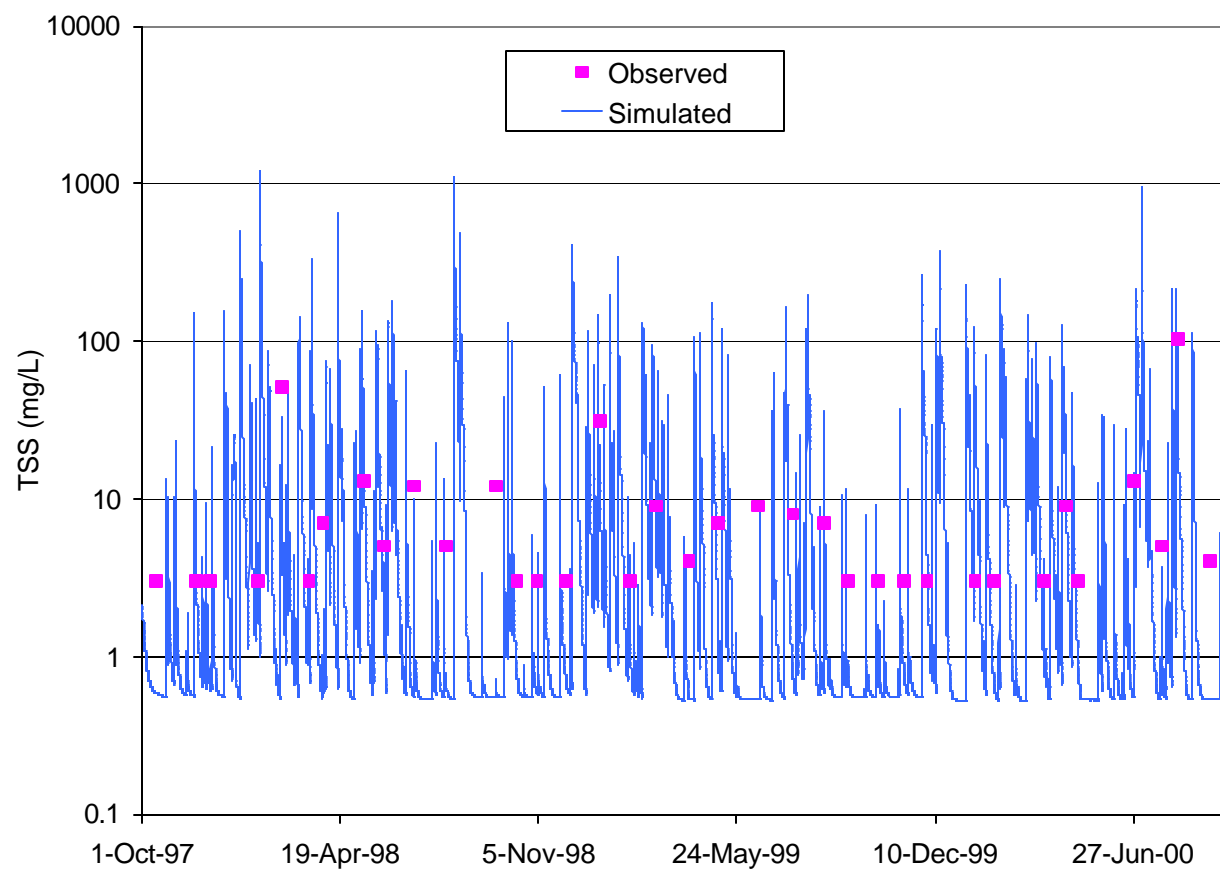


Figure B. 11 Observed and simulated sediment concentration (TSS/100 mL) at DEQ station 6CNFH089.25.

Table B. 10 Observed and simulated sediment concentration statistics during calibration period.

Station	Observed (mg/L)			Simulated (mg/L)			Mean Standard Error (mg/L)
	Geometric Mean	Minimum	Maximum	Geometric Mean	Minimum	Maximum	
6CNFH008.78	7.9	3	97	3.1	0.8	698	0.57
6CNFH059.65	5.4	3	103	3.1	1	926	0.39
6CNFH089.25	5.7	3	103	2.0	0.5	1,135	0.35

The sediment validation was conducted for the time period from 10/01/1994 to 9/30/1997. The results of sediment validation are shown in Figures B.12 through B.14 and Table B.11.

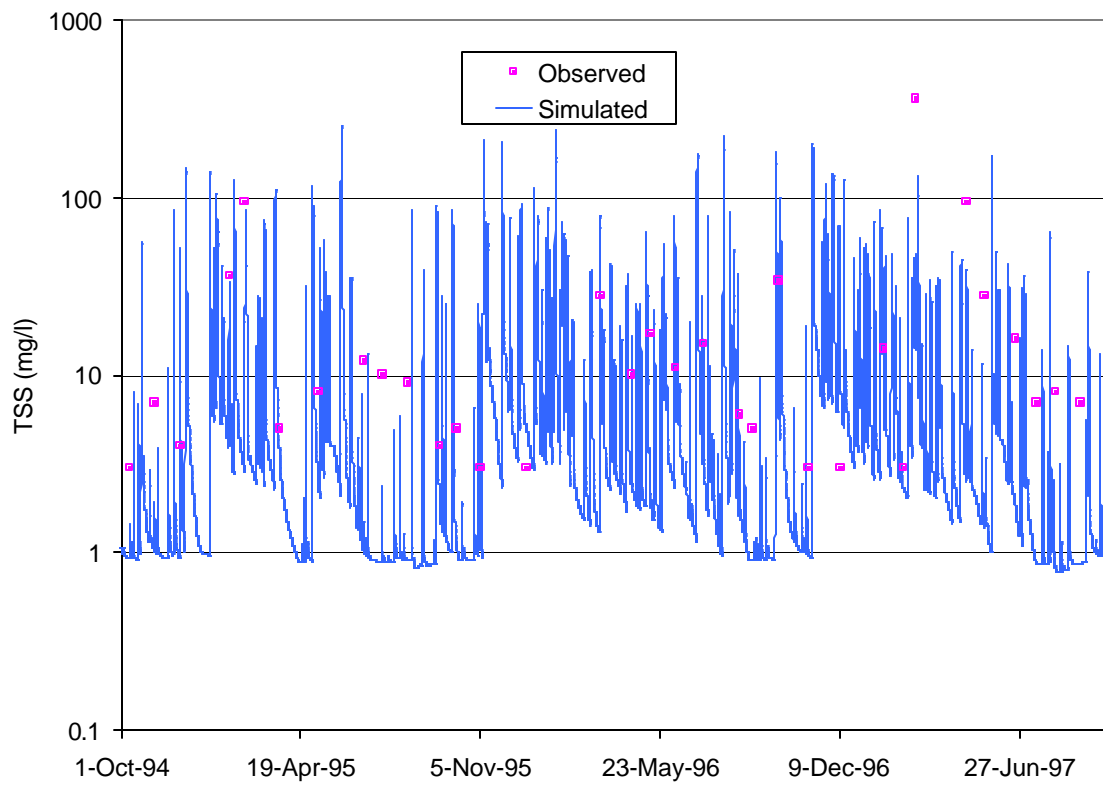


Figure B. 12 Observed and simulated sediment concentration (TSS/100 mL) at DEQ station 6CNFH008.78 during validation period.

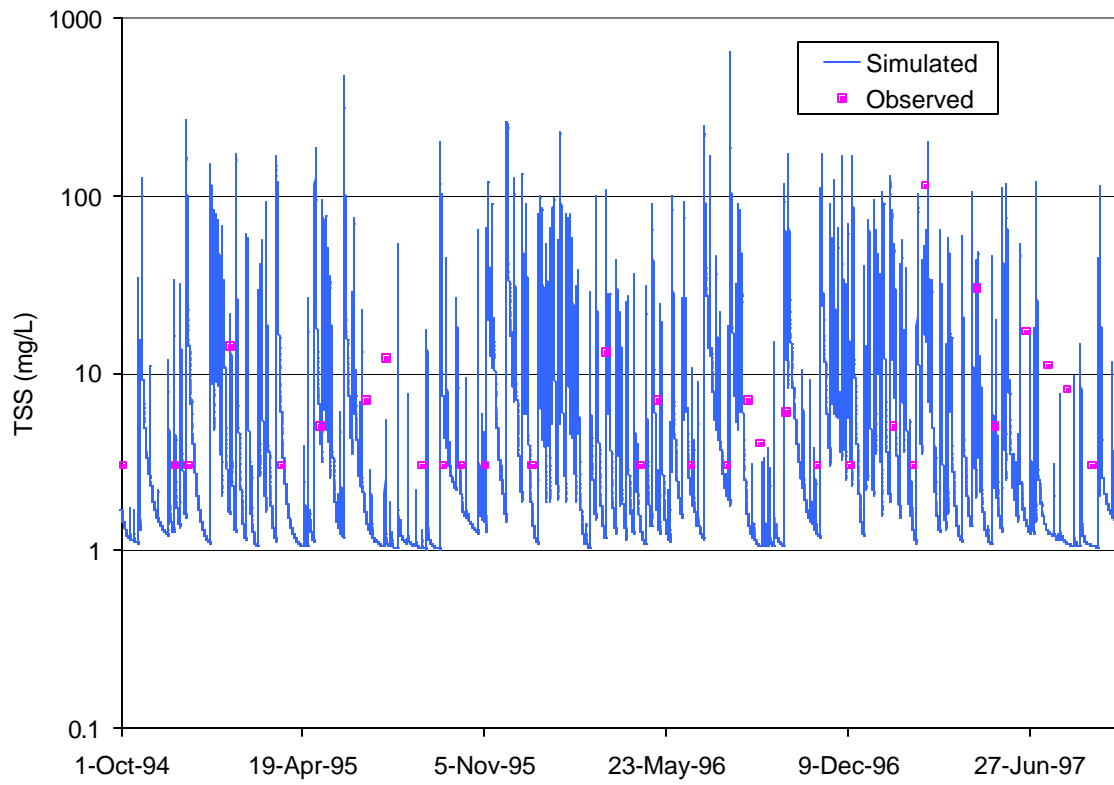


Figure B. 13 Observed and simulated sediment concentration (TSS/100 mL) at DEQ station 6CNFH059.65 during validation period.

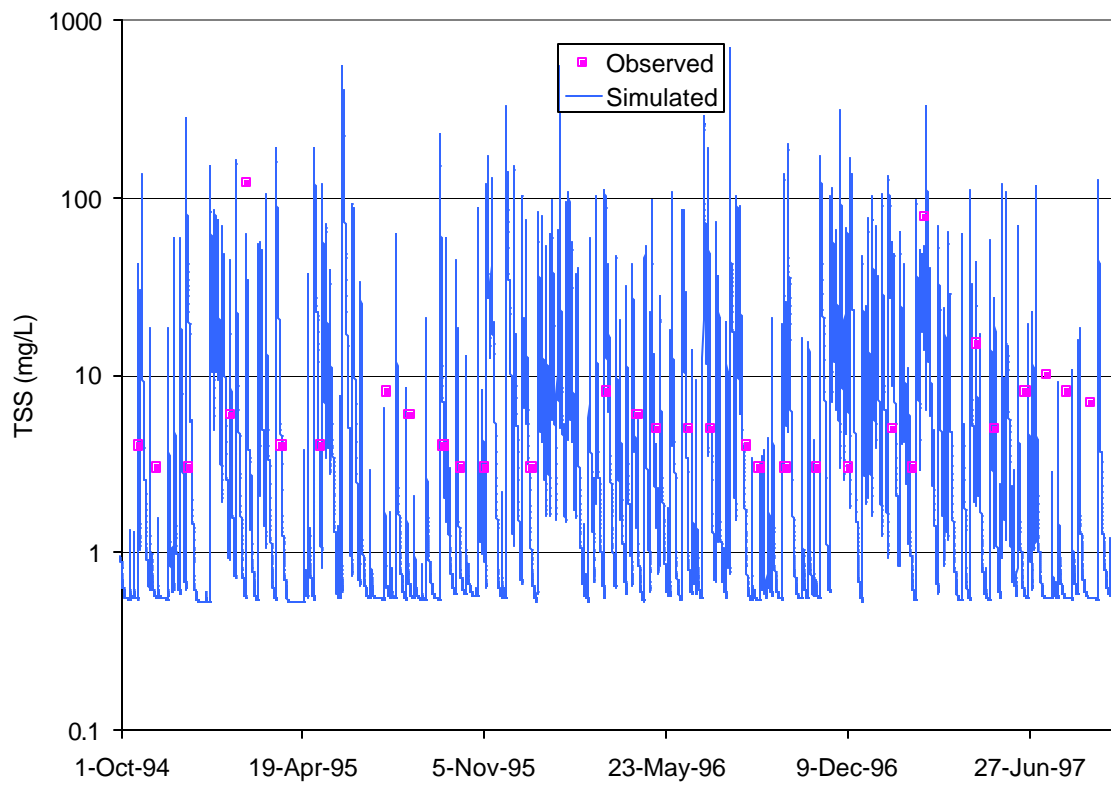


Figure B. 14 Observed and simulated sediment concentration (TSS/100 mL) at DEQ station 6CNFH089.25 during validation period.

Table B.11 Observed and simulated sediment concentration statistics during validation period.

Station	Observed (mg/L)			Simulated (mg/L)			Mean Standard Error (mg/L)
	Geometric Mean	Minimum	Maximum	Geometric Mean	Minimum	Maximum	
6CNFH008.78	10.4	3	362	3.4	0.8	250	1.5
6CNFH059.65	5.5	3	114	3.6	1	585	0.4
6CNFH089.25	5.7	3	121	2.4	0.5	648	0.4

Total Mercury Model Calibration/Validation

The last stage of model calibration deals with calibrating total mercury. All quantified sources were included in the mercury transport model. The period selected for model calibration was dictated by the in-stream observed data collected at several locations along the NFHR during 2008. The sampling was conducted monthly from April to September, 2008 at several locations that were all on the NFHR.

The mechanisms of mercury entry into streams accounted for in this study included direct atmospheric deposition on water surface, interflow and groundwater, point sources, and via sediment attached. Model parameters adjusted during calibration included adsorption coefficient (KD) and phase transfer rate coefficient (ADRATE). In addition, the interflow and groundwater concentration were also adjusted. A monitoring site that was located near river mile 84 was used to calibrate the background conditions since it was upstream of the location of the chlorine plant.

The final value of adsorption coefficient (KD) was 1.0 and phase transfer rate (ADRATE) was 20. Figures B.15 through B.22 show the simulated hourly concentration, simulated 90-day rolling median, and observed values at each location. Table B.12 shows a comparison between the medians of simulated and observed concentrations at the eight monitoring locations. The visual comparison, along with the median comparison, shows a good model agreement.

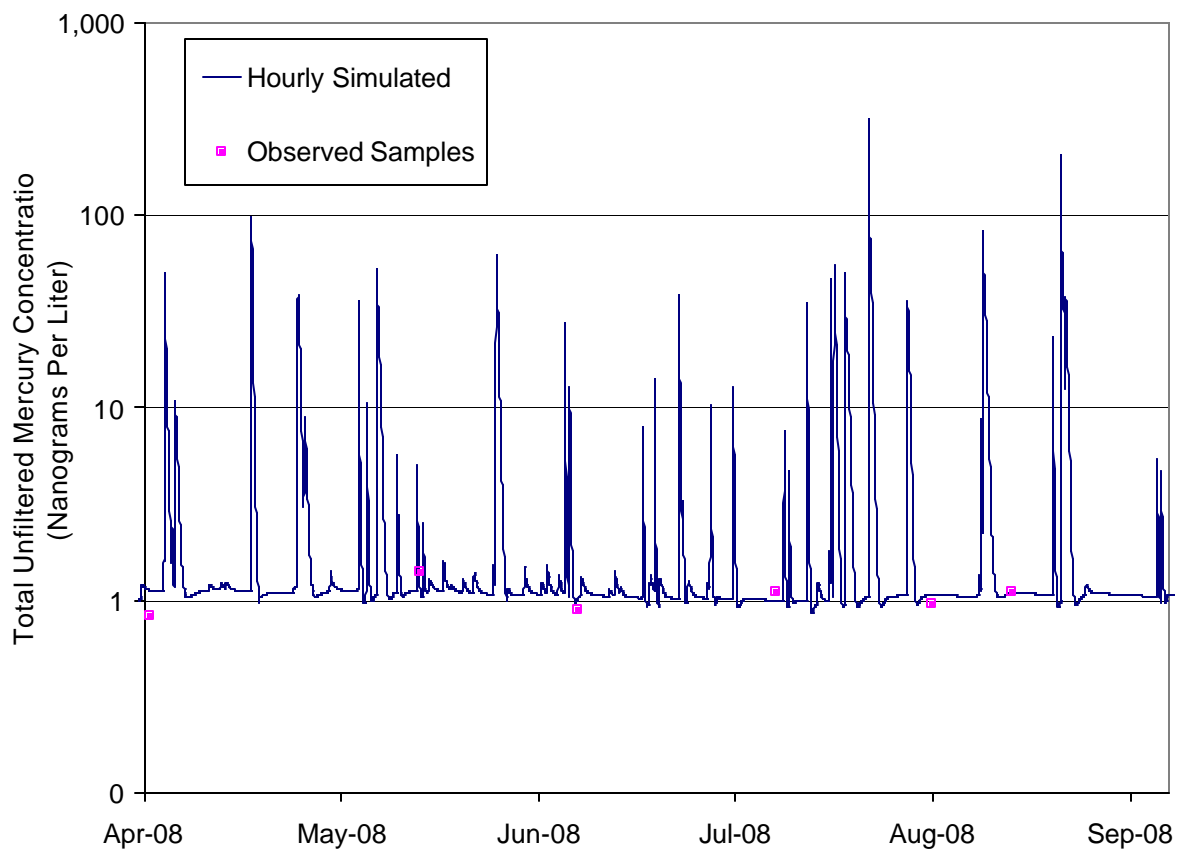


Figure B. 15 Simulated and observed total unfiltered mercury concentration at river mile 84.3 for the calibration period of 4/1/2008 to 9/30/2008.

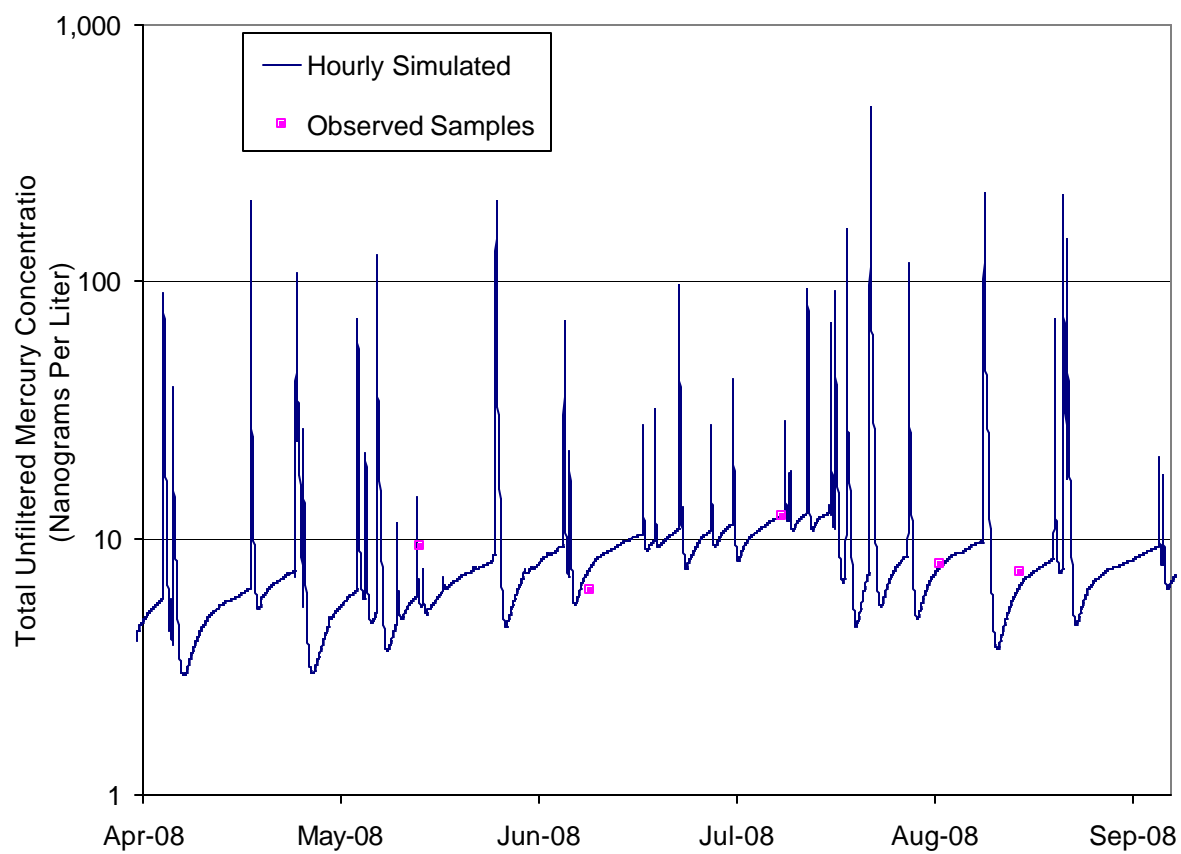


Figure B. 16 Simulated and observed total unfiltered mercury concentration at river mile 80.1 for the calibration period of 4/1/2008 to 9/30/2008.

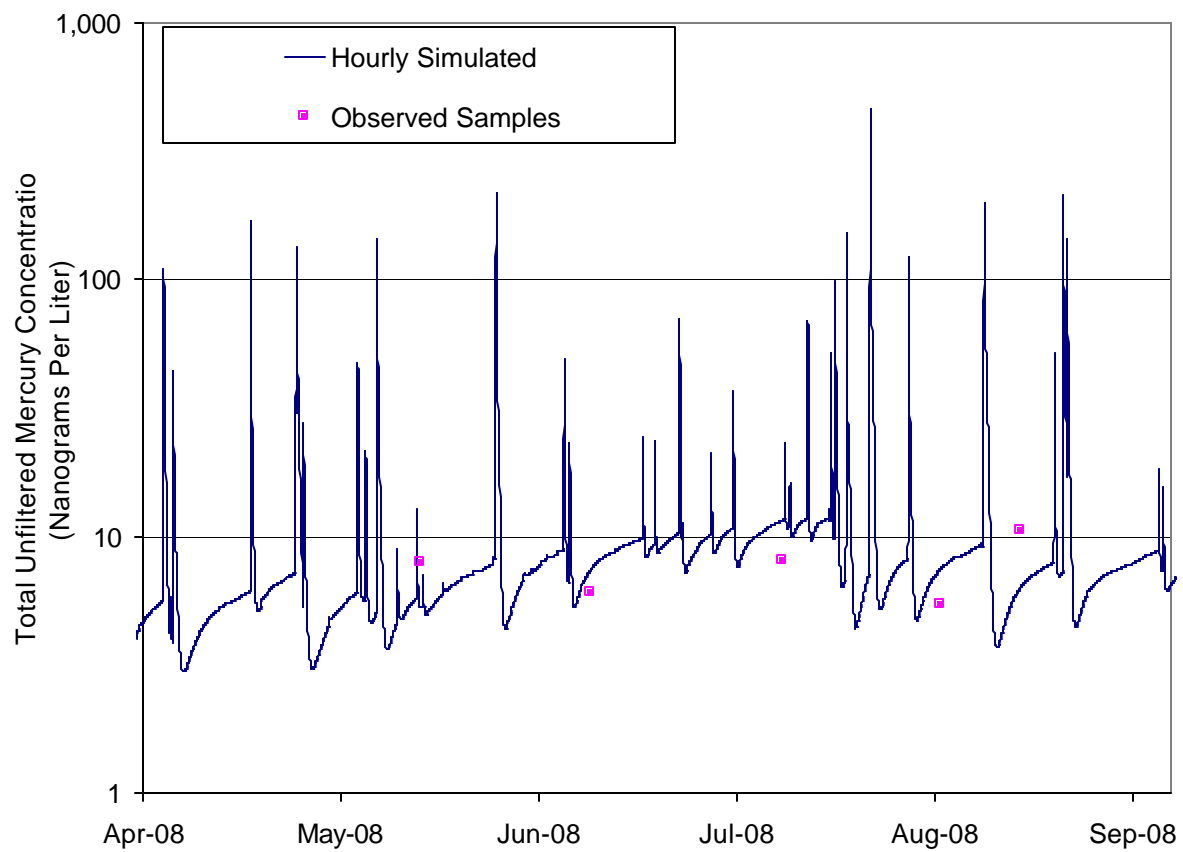


Figure B. 17 Simulated and observed total unfiltered mercury concentration at river mile 76.9 for the calibration period of 4/1/2008 to 9/30/2008.

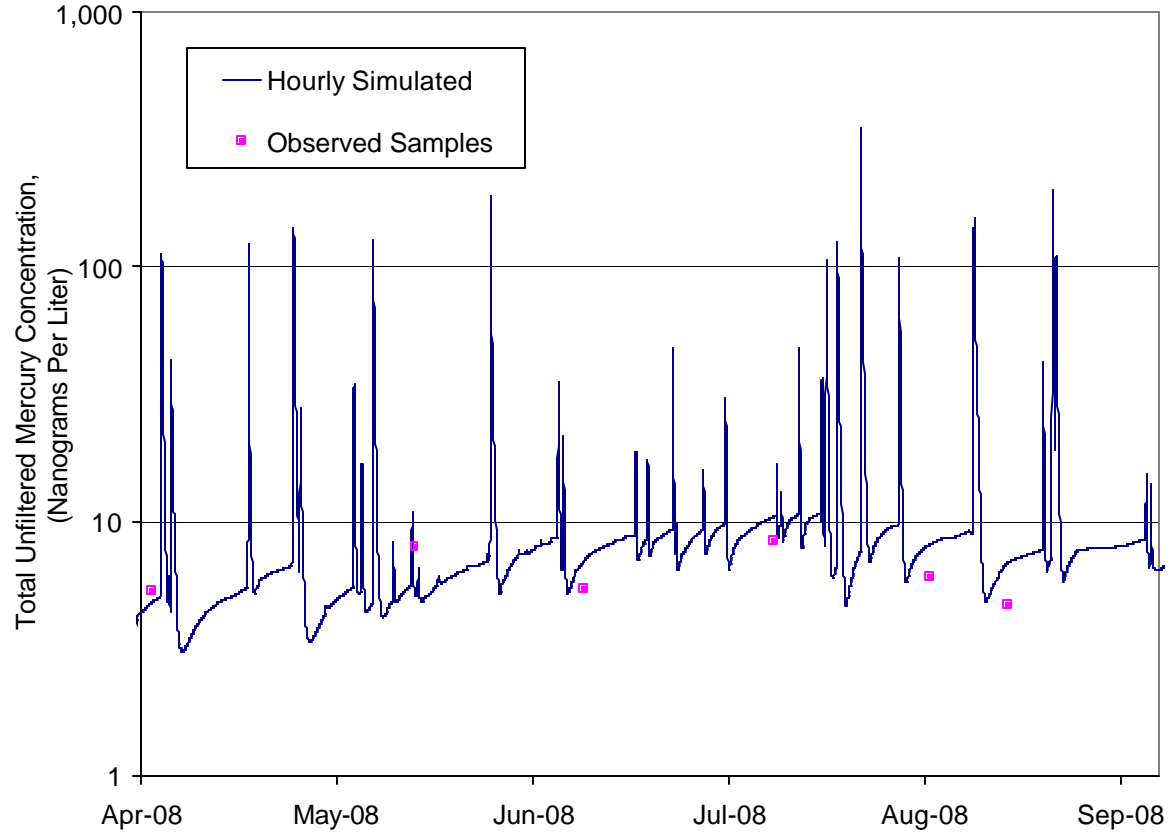


Figure B. 18 Simulated and observed total unfiltered mercury concentration at river mile 72.3 for the calibration period of 4/1/2008 to 9/30/2008.

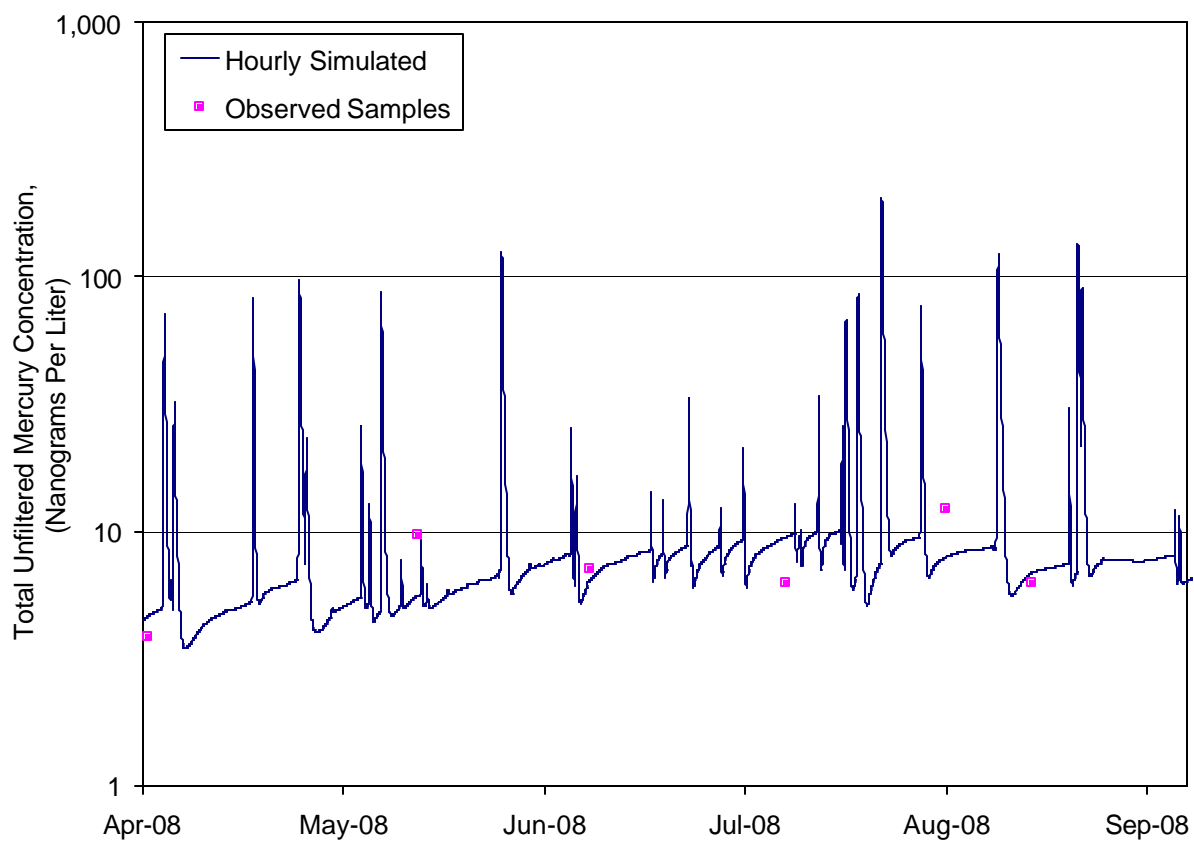


Figure B. 19 Simulated and observed total unfiltered mercury concentration at river mile 69.9 for the calibration period of 4/1/2008 to 9/30/2008.

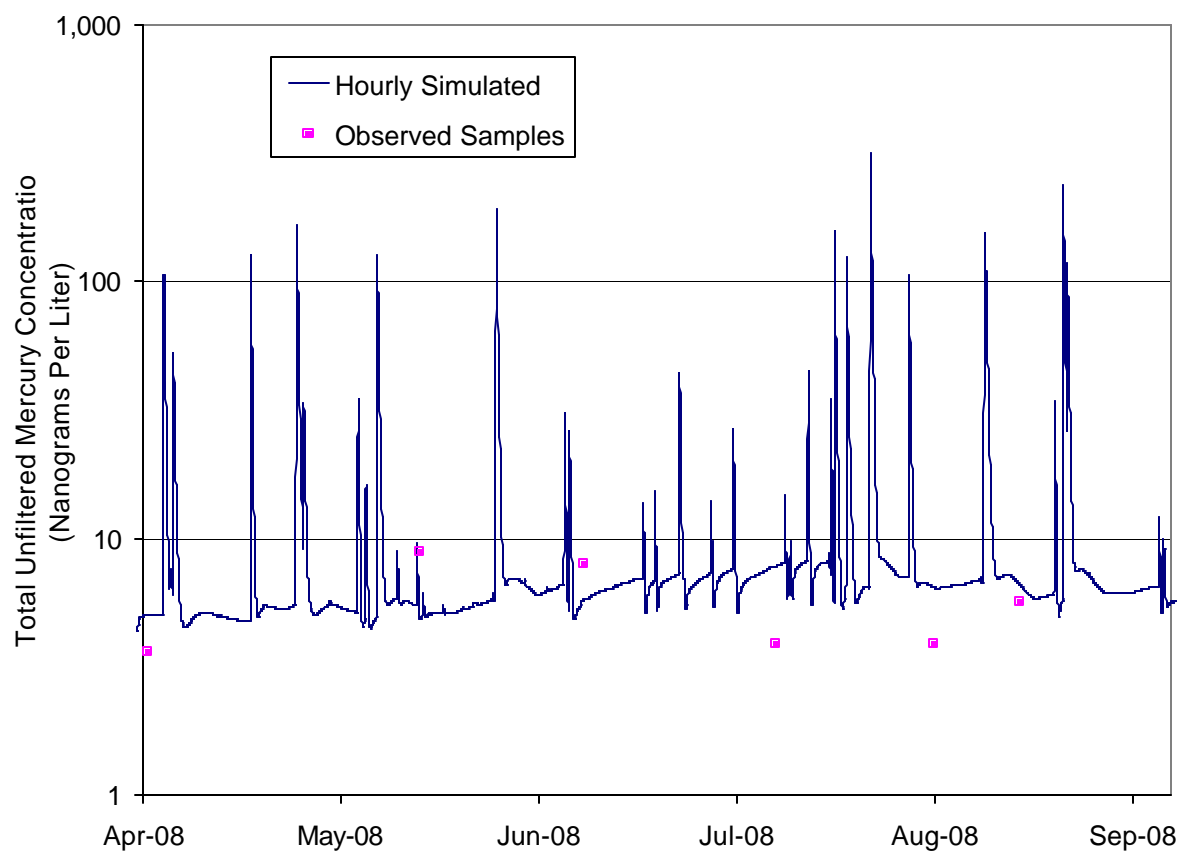


Figure B. 20 Simulated and observed total unfiltered mercury concentration at river mile 60.7 for the calibration period of 4/1/2008 to 9/30/2008.

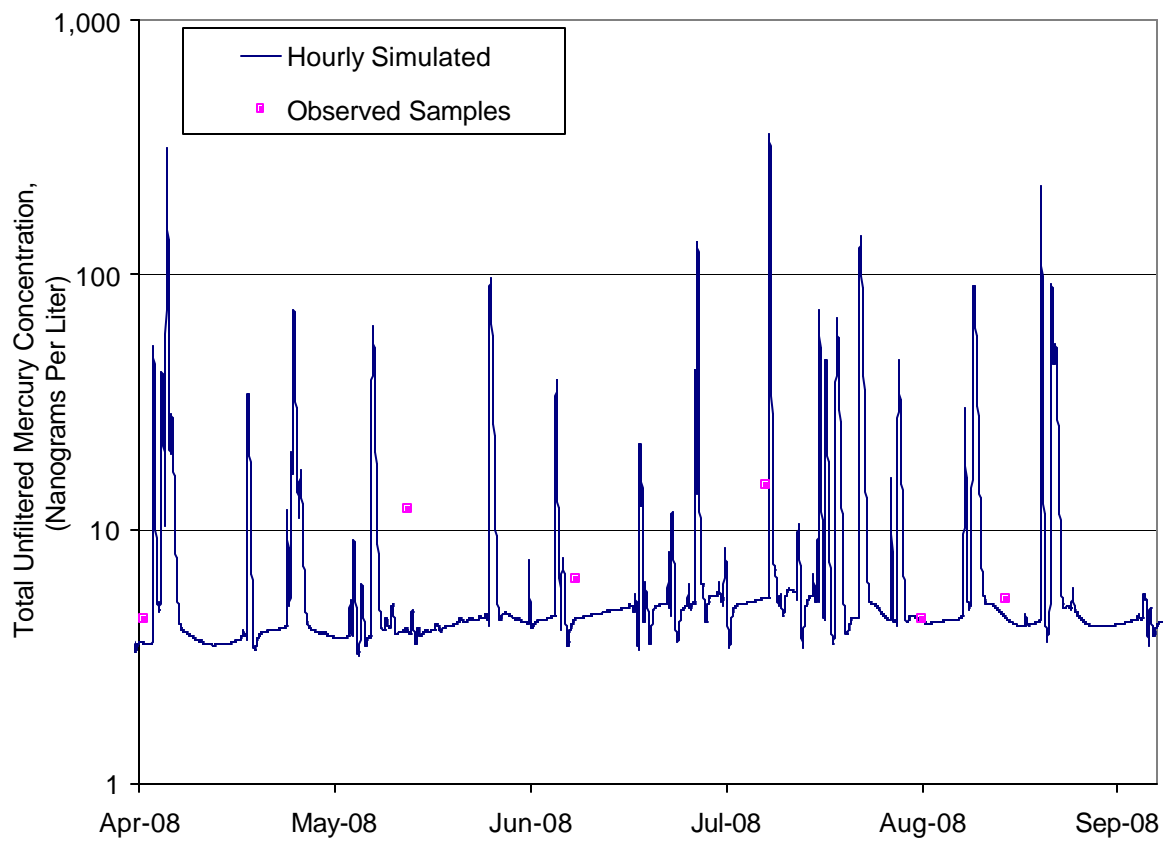


Figure B. 21 Simulated and observed total unfiltered mercury concentration at river mile 22.1 for the calibration period of 4/1/2008 to 9/30/2008.

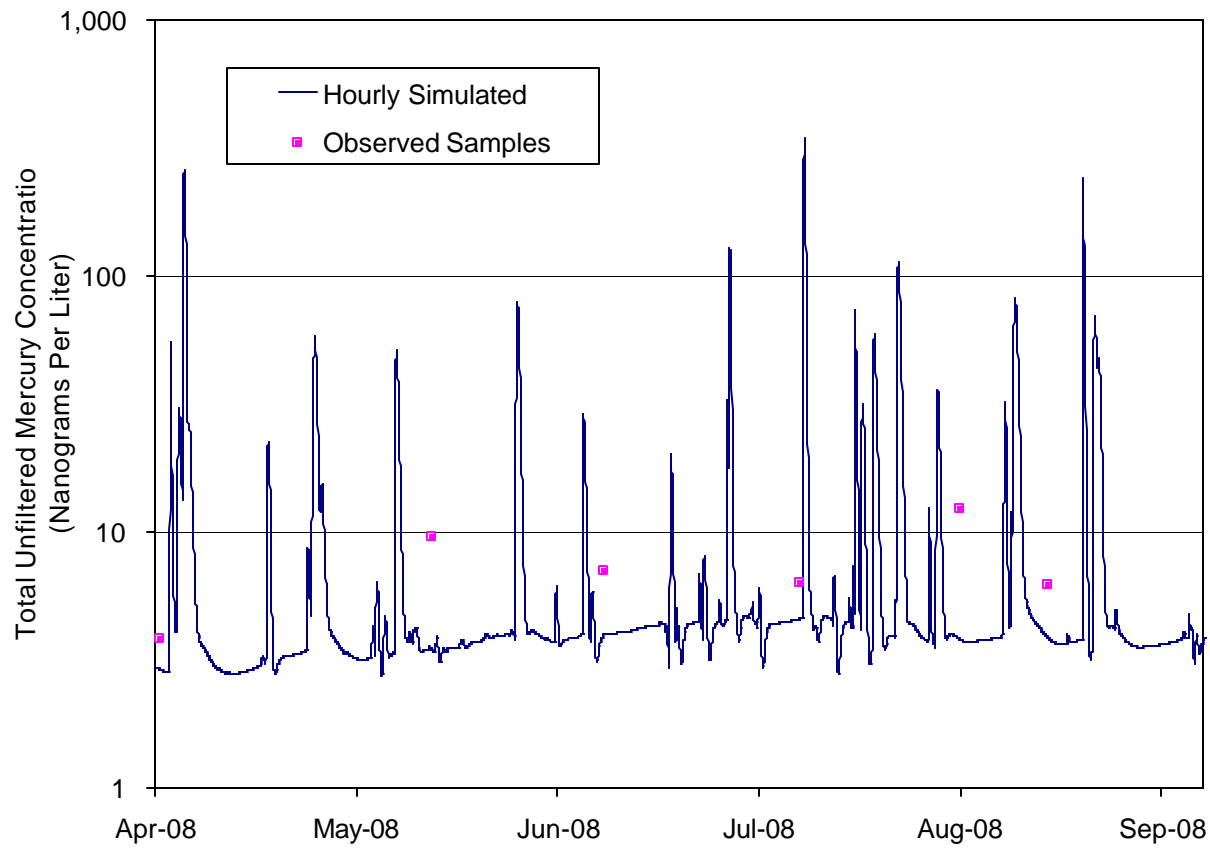


Figure B. 22 Simulated and observed total unfiltered mercury concentration at river mile 8.8 for the calibration period of 4/1/2008 to 9/30/2008.

Table B. 12 Median of observed and predicted total mercury concentrations for calibration period.

River Mile	Median of Observed Samples (ng/L)	Median of Simulated Hourly Concentrations (ng/L)
RM 84.3	1.0	1.1
RM 80.1	8.0	7.6
RM 76.9	8.0	7.3
RM 72.3	5.7	4.4
RM 69.9	6.0	7.3
RM 60.7	4.8	6.4
RM 22.1	5.9	4.5
RM 8.8	6.7	3.9